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WOOD DISTILLATION

BY

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American Chemical Society
Monograph Series

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GENERAL INTRODUCTION

American Chemical Society Series of Scientific and Technologic Monographs

By arrangement with the Interallied Conference of Pure and Applied Chemistry, which met in London and Brussels in July, 1919, the American Chemical Society was to undertake the production and publication of Scientific and Technologic Monographs on chemical subjects. At the same time it was agreed that the National Research Council, in coöperation with the American Chemical Society and the American Physical Society, should undertake the production and publication of Critical Tables of Chemical and Physical Constants. The American Chemical Society and the National Research Council mutually agreed to care for these two fields of chemical development. The American Chemical Society named as Trustees, to make the necessary arrangements for the publication of the monographs, Charles L. Parsons, Secretary of the American Chemical Society, Washington, D. C.; John E. Teeple, Treasurer of the American Chemical Society, New York City; and Professor Gellert Alleman of Swarthmore College. The Trustees have arranged for the publication of the American Chemical Society series of (a) Scientific and (b) Technologic Monographs by the Chemical Catalog Company of New York City.

The Council, acting through the Committee on National Policy of the American Chemical Society, appointed the editors, named at the close of this introduction, to have charge of securing authors, and of considering critically the manuscripts prepared. The editors of each series will endeavor to select topics which are of current interest and authors who are recognized as authorities in their respective fields. The list of monographs thus far secured appears in the publisher's own announcement elsewhere in this volume.

The development of knowledge in all branches of science, and especially in chemistry, has been so rapid during the last fifty years and the fields covered by this development have been so varied that it is difficult for any individual to keep in touch with the progress in branches of science outside his own specialty. In spite of the facilities for the examination of the literature given by Chemical Abstracts and such compendia as Beilstein's Handbuch der Organischen Chemie, Richter's Lexikon, Ostwald's Lehrbuch der Allgemeinen Chemie, Abegg's and Gmelin-Kraut's Handbuch der Anorganischen Chemie and the English and French Dictionaries of Chemistry, it often takes a great deal of time to coördinate the knowledge available upon a single topic. Consequently when men who have spent years in the study of important subjects are willing to coördinate their knowledge and present it in concise, readable form, they perform a service of the highest value to their fellow chemists.

It was with a clear recognition of the usefulness of reviews of this character that a Committee of the American Chemical Society recommended the publication of the two series of monographs under the auspices of the Society.

Two rather distinct purposes are to be served by these monographs. The first purpose, whose fulfilment will probably render to chemists in general the most important service, is to present the knowledge available upon the chosen topic in a readable form, intelligible to those whose activities may be along a wholly different line. Many chemists fail to realize how closely their investigations may be connected with other work which on the surface appears far afield from their own. These monographs will enable such men to form closer contact with the work of chemists in other lines of research. The second purpose is to promote research in the branch of science covered by the monograph, by furnishing a well digested survey of the progress already made in that field and by pointing out directions in which investigation needs to be extended. To facilitate the attainment of this purpose, it is intended to include extended references to the literature, which will enable anyone interested to follow up the subject in more detail. If the literature is so voluminous that a complete bibliography is impracticable, a critical selection will be made of those papers which are most important.

The publication of these books marks a distinct departure in the policy of the American Chemical Society inasmuch as it is a serious attempt to found an American chemical literature without primary regard to commercial considerations. The success of the venture will depend in large part upon the measure of coöperation which can be secured in the preparation of books dealing adequately with topics of general interest; it is earnestly hoped, therefore, that every member of the various organizations in the chemical and allied industries will recognize the importance of the enterprise and take sufficient interest to justify it.

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Introduction.

Literature on wood distillation in book form and in English has been very meagre. The only book dealing solely with this subject is Harper's "Utilization of Waste Wood by Distillation" and this is not much more than a compilation of patent specifications without stating whether the processes described had ever been used commercially. It also dealt mainly with resinous wood distillation and hardwoods were treated only briefly. In chapters of other books wood distillation has been covered briefly. In the English translation of Dusnesny and Noyers "L'Industrie Chimique du Bois," 1908, is included a general description of the industry which according to Klar is taken largely from his first edition of "Technologie der Holzverkohlung." In Brown's "Forest Products," 1917, one chapter gives a good but brief general description. The New York State Forest School booklet on "The Hardwood Distillation Industry in New York," also by Brown, is good but it is written by a forester not a chemist. In Roger's "Industrial Chemistry" the chapter on wood distillation by Harper is full of errors.

In foreign languages two good books have appeared. The first edition of Klar's "Technologie der Holzverkohlung" appeared in 1903 and a much enlarged second edition came out in 1910. Klar has had much experience in building wood distillation apparatus and much of his information is first hand. The work is very complete and contains many chemical engineering details. Besides the primary crude products of hardwood distillation the methods of production of the secondary products, acetic acid, acetone, and formaldehyde, are also described. The destructive distillation of resinous wood is also covered. This work, however, deals largely with European practice and is rapidly becoming out of date, especially on the chemical, scientific side.

The latest book on the subject is "Om Träkolning" by Bergström and Wesslen, 1918. This gives a very good and complete description of Swedish practice and contains the results of much experimental work not previously published. It abounds in illustrations, tables, diagrams and curves, so that it is interesting even to a reader who knows little Swedish.[1]

Both these books have been frequently drawn on in the preparation of this monograph but proper credit has been given in every instance and the thanks of the author are here rendered for the assistance.

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[1] Although it is not strictly wood distillation as limited in this monograph attention is called to the very complete description of the construction and operation of various types of charcoal kilns found in this book. It is the only detailed and satisfying treatment of the subject that the writer has seen.

In this monograph the two very distinct industries of hardwood distillation and resinous wood distillation have been kept entirely separate in Parts I and II, respectively. In this country there is absolutely no connection between the two except that they both use wood as a raw material (very different kinds of wood, however) and both produce charcoal (only a part of the resinous wood industry produces charcoal). In Sweden the two are so closely related that they can not be readily treated separately but in describing the commercial practice in this country only confusion results from attempts to combine them.

The arrangement of the subject matter is perhaps peculiar. The first chapter of each part is a general description of commercial practice without any detailed discussion. These are only outlines on which to hang the main part of the book which is a discussion of the chemistry of the raw material, the process, and the products.

Although an engineering phase of the subject is only occasionally discussed, it is believed that the chemical engineer and plant operator will still find the book interesting since it gives fundamental information on the chemistry of the process so that they may get a suggestion as to what may be the result of any change in the conditions of operation. The chemical student and research man should find many points of interest especially since the lack of information on some important subject is frequently pointed out.

Only the methods of producing the crude products of hardwood distillation are included and formaldehyde, acetic acid and acetone are not mentioned. Refined wood alcohol is treated very briefly. This is on account of disinclination to copy from the literature without that first-hand information which gives the necessary skill in selection and criticism.

The author's contact with the industry has been largely the result of his connection with the Forest Service and the Forest Products Laboratory which has made possible frequent inspections of commercial plants and a large amount of research on the general subject. It will be noted that many of the literature references are to publications from the Laboratory and that many of the illustrations are taken from these publications.

The author wishes to thank the following firms for their kindness in furnishing cuts and figures of plants and apparatus: The Newport Turpentine and Rosin Company, The Struthers-Wells Company, Florida Wood Products Company, Hercules Powder Company, and The Tennessee-Eastman Corporation.

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Chapter I.

The Commercial Processes.

The hardwood distillation industry was developed early in the United States on account of the large supplies of good quality hardwoods available and on account of the high excise tax on ethyl alcohol which forced the use of wood alcohol for solvent purposes where the cheaper ethyl alcohol might otherwise have been used. Even since the denatured alcohol legislation of 1906 which made available the cheaper denatured ethyl alcohol for solvent purposes, the industry has expanded due to the increased demands for methyl alcohol as a chemical raw material and for the other products, acetate of lime and charcoal.

The early industry used either the small horizontal cylindrical retorts or the brick by-products kilns for the distillation of the wood, but for many years no new plants have been built with either of these types of distillation apparatus. Many of the old retort or kiln plants have been replaced by the modern type of plant but some of them are still in operation. The main objection to the retorts was the high labor costs for charging the wood and removing the charcoal, these operations being carried out entirely by hand. The kilns which gave low yields of the chemical products were used only in connection with iron furnaces where large quantities of charcoal were required and the chemical products were of secondary importance. When the chemical products became of more importance no more kiln plants were built. In the following general description of the plant and operation only the modern type of distillation apparatus, the rectangular oven, will be included.

Wood for Distillation

The wood used for distillation is generally cordwood 52 inches long and with a minimum diameter of 3 to 5 inches varying with the conditions of supply and demand. Sticks of greater diameter than about 8 inches are usually split. Some sawmill slabs or other wood wastes are used in which case smaller dimensions in length and thickness are allowed. Small blocks, chips, shavings or sawdust are not used. The source of the wood varies; in some cases the wood distillation plant is run in connection with a sawmill and the logging wastes such as tops and limbs are gathered and cut for distillation. In other cases the distillation wood is the main product obtained from the forest and the sawmill operation may be secondary or lacking entirely. This usually takes place where the timber is small second growth or of poor quality for lumber. Most of the plants own or control their own wood supply and cut and collect their own wood or have a contract with a sawmill for waste wood, but some of the smaller plants purchase a part of their wood already cut.

The wood is not generally selected by species except that softwoods are excluded. All the hardwoods which naturally occur in the forests where the wood is cut are commonly collected, since the main species are satisfactory and the others occur in too small quantities to have much effect on the results. In the north the main species are beech, birch and maple, but other species which may occur with them such as elm, ironwood, oak, ash, etc., are used. In the south oak and hickory are the favorite species and some selection may be resorted to in order to eliminate such undesirable hardwoods as chestnut.

The wood is dried for six to eighteen months either in the woods where cut or in storage yards at the plant. It is not required to have the wood completely dry and "air dry" wood with 15 to 20 per cent moisture is considered satisfactory. If the wood is dried in the woods where cut the drying is slow and there is a good chance for deterioration by rotting and danger from fire, whereas if dried in the wood yard there is an extra expense of handling to and from the piles. In either case the interest charge on the investment in a year's supply of wood is an important item of expense. In order to avoid these difficulties connected with air drying a system of artificial drying has been developed and adopted by several plants. The wood dries much faster when in short lengths and so for artificial drying the sticks are preferably cut into blocks 6 to 10 inches long. These blocks are run by conveyor from the saws to the cars in which they are distilled and no further handling is required. It is a general rule that the smaller the pieces of wood which go to make up a pile the less wood can be contained in a given space, but when blocks 6 inches long are dropped from a hopper into a car a greater weight of wood is put in than when 52 inch sticks are piled by hand in the same car. This is another advantage of the artificial drying system. The cars and the wood being hot at the time they enter the retort also has a little effect on the time and fuel required for distillation.

The artificial drying is accomplished by the waste heat from the flues of the retort furnaces. The cars of wood are placed in closed "pre-driers" and the flue gases from the retorts are blown into the driers in direct contact with the wood. Care must be taken that the

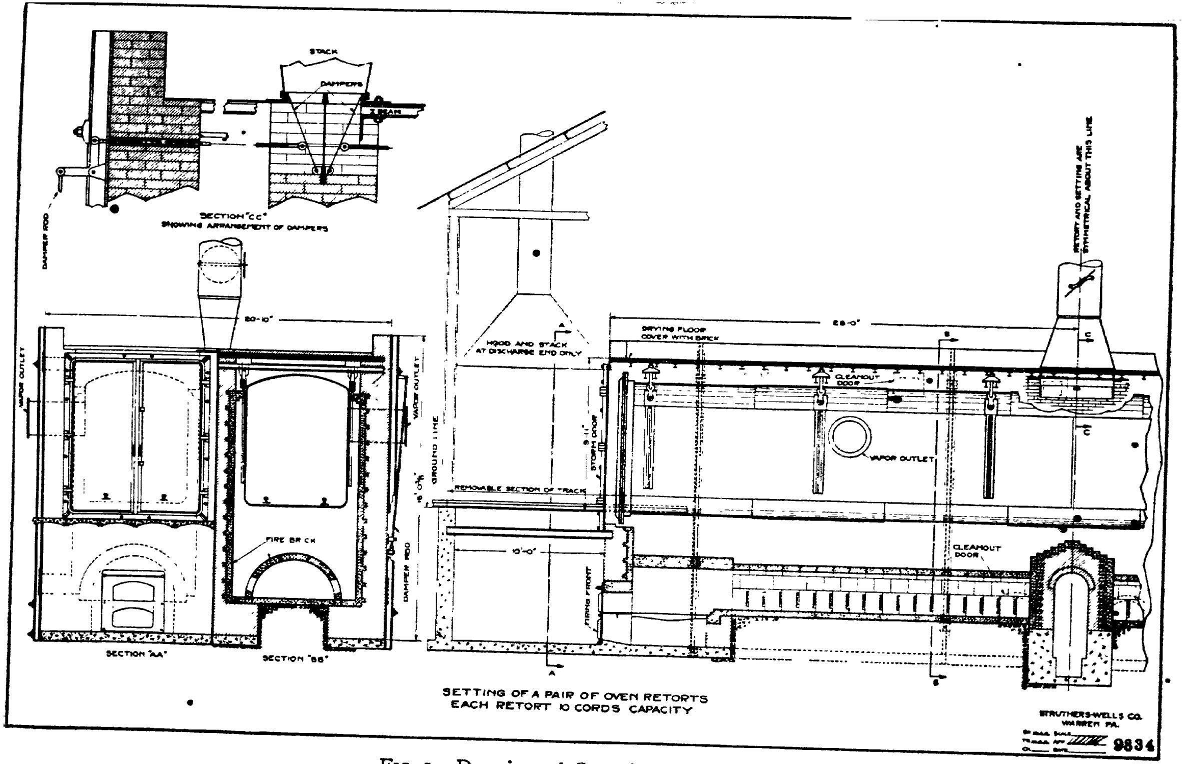

FIG. 1.—Drawing of Oven in Brick Setting.

temperature of the incoming gases is not too high and that sparks do not carry through to the wood. Otherwise, the process is nearly automatic. Commonly three charges of wood are in the driers at one time, the wood from the hot end of the drier being drawn direct to the retort while a fresh charge of green wood is introduced at the cold end.

The Distillation of the Wood

The large rectangular retorts commonly used for the distillation of the wood are frequently called ovens or "Jumbos" to distinguish them from the older, smaller, cylindrical retorts. These ovens are commonly made of flange steel 3/8″ thick with somewhat thicker metal on the bottom where the temperature is highest. They are 6′ 3″ wide and 8′ 4″ high and vary in length according to the capacity desired, the standard 10 cord oven being 56′ long. The oven doors open the full cross section and are fastened by steel wedges. Since the doors are the only surfaces of the retorts not directly heated they are usually provided with outside "storm doors" to prevent radiation and condensation of tar on their inner surfaces. On account of the great length of the oven and the difference in expansion with heat between steel and brickwork the ovens can not be supported at the bottom on brick but are suspended from hangers along the top of the sides. (See Fig. I.) The ovens are heated from fire boxes at one end in the case of the shorter ovens or at both ends in the case of the longer ones. In order to distribute the heat evenly throughout the length of the ovens special arches must be provided. These brick arches in the case of two fire boxes run from the fire boxes nearly to the center of the oven and prevent direct contact of the flames on the bottom of the oven. By properly spaced openings in the arches the flames or the hot flue gases are distributed lengthwise and sidewise so as to distribute the heat over the bottom of the retort as evenly as is practicable. The flue gases are then guided around the sides of the retort by suitable baffles, finally passing over the top and thence up the stack. Even with this arrangement the equalization of the heating is not complete and the bottom of the retort commonly gets the highest temperature. The ovens are set in pairs with the brickwork for the two continuous although there is no connection between the fire boxes. The space between each pair is thus utilized for condensers, piping, etc.

The wood is loaded on iron cars or "buggies" with slatted ends and sides, the latter sometimes reaching only about two-thirds of the height of the piled wood and serving to retain the charcoal after carbonization. The sides are also removable for loading the wood and unloading the charcoal. The cars very nearly fill the cross section of the retort and are long enough to hold about 2½ cords, four cars making one charge for a 10 cord retort. The cars are sometimes moved by hand but usually with a power cable or a small locomotive.

As soon as the wood is inside the retort the doors are closed and the heating started. The first distillate is almost entirely water and it is not until about the fourth hour that the liquor slowly darkens and contains increasing amounts of acid. The tar first appears at the eighth to tenth hour and from this time onward very little more heat is required to finish the distillation at about the twenty-second hour. For about two hours the retort is allowed to cool and then the charcoal is removed and a new charge of wood run in, making a complete cycle in 24 hours. The time for a complete cycle may vary at different plants depending on the moisture condition of the wood, the kind of fuel used or the desire of the operator, but a 24 hour cycle is common. One plant operated for some time on a 16-18 hour cycle and thus greatly increased the capacity of the retorts.

FIG. 2 Photo of Oven in Shop

Various methods are used to control the firing, the appearance of the distillate and the temperature in the vapor outlet from the retort being the most common signs for determining the status of the distillation. It is usually required to finish the distillation in a certain definite time and without too rapid heating or too high a temperature during the stage when the valuable products are distilling. To accomplish this the charge is heated rapidly at the start and then at the proper time, usually eight to ten hours from the start, the firing is cut down so that the distillation will not "run away" or become uncontrollable.

Tar and gas from the plants' own products are generally used for retort fuel and besides these only a small amount of other fuel is required. If the tar or gas is used for boiler fuel other fuel as coal, natural gas or waste wood is used. One plant has used hogged sawmill waste almost entirely as a retort fuel by modifying the ordinary fire box into a small Dutch oven for the more efficient use of this kind of fuel. The wood tar and natural gas make excellent fuel because they both give a quick, hot fire and yet can be readily regulated.

The hot charcoal from the retorts catches fire as soon as it comes in contact with the air and it must, therefore, be cooled out of contact with the air. Closed charcoal coolers are provided into which the cars of charcoal are run as rapidly as possible after the retorts are opened, a spray of water being used to keep down the fire a little during the transfer. The charcoal stays in this cooler until another distillation cycle is finished and then it is moved on to the next. It remains there for 24 hours and then is allowed to stand in the cars in the open air for another 24 hours before it will be received for shipment by the railroads. The coolers are of the same shape and size as the ovens but are built of lighter metal and sometimes are without a bottom, being banked with sand to prevent access of air.

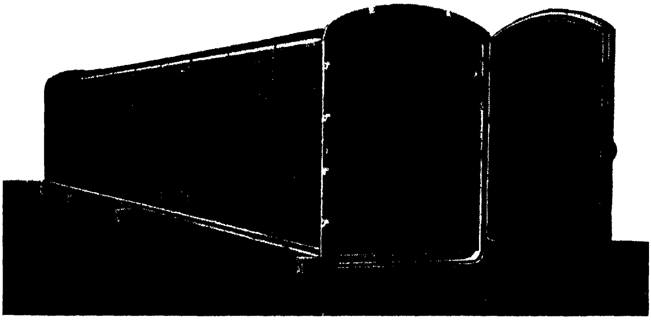

Fig. 3.--Photo of Cooler in Shop.

The best layout for the wood yard, retort house, coolers and charcoal sheds is one in which the progress of the cars is in one direction throughout the operation. (See Fig. 4.) In some cases lack of space makes this layout impossible and the retorts may be charged and discharged at the same end. It is almost a necessity, however, that the first coolers be in line with the retorts so that the hot charcoal may be moved rapidly.

The vapors are taken from the retort through one to three outlets, depending on the size of the retort. Ordinarily only two outlets are used, even on the 10 cord retorts. The vapor outlets are on the sides of the retorts near the top and pass through the brickwork to the condensers. The condensers are of the vertical tubular type and they must have a capacity to condense and cool the vapors during the peak load, although this may cover only a small part of the distillation period. The inside of the condenser tubes should also be readily accessible, since it is necessary frequently to clean out the tubes to remove deposits of pitch and tar which greatly decrease the efficiency of the condenser. At many plants the retort condenser tubes are cleansed regularly once a week.

At the condenser outlet the liquid distillate is separated from the gas by means of a simple gooseneck or trap which allows the liquid to flow through but stops the gas. The gas is taken off at the top of the trap on the end toward the condenser and piped to the retort fire box or to the boilers. No storage is provided for the gas and it is burned as it is produced. A valve in the gas line from each condenser is usually closed when no gas is coming off from the retort.

Refining Processes

The liquid distillate, consisting of tar and a dark brown watery liquid called pyroligneous acid, is pumped to wooden settling tanks where the tar settles to the bottom. These tanks are usually arranged in series with connecting pipes at gradually lower levels from the first, where the mixture of tar and pyroligneous acid enters, to the last, where the clear acid is drawn off for further refining. The tar is drawn off as required from the bottom of each tank, most of it naturally coming from the first.

Although most of the valuable products, wood alcohol and acetic acid, is contained in the pyroligneous acid, yet there are small quantities contained in the tar which is distilled with steam for their recovery. A wooden still is used for this operation, since copper is so rapidly corroded by the hot tar. The still is provided with a closed steam coil of copper and also with a steam jet. The water in the tar is driven off by heating with the closed coil and then live steam is blown through the tar. The volatile oils from the tar are distilled with the steam and are separated from the water layer by settling. The first oils distilled are lighter than water, but if the distillation is carried far enough oils heavier than water will distil. Sometimes these oils are kept separate as part of the marketable products, but frequently they are mixed with the residue left in the tar still and used for fuel. The water distillate from the tar still contains acetic acid and alcohol and is mixed with the similar distillate from the next operation.

The pyroligneous acid from the settling tanks, although it has been settled free from suspended tar, still contains some tar in solution which must be separated in the first refining operation. This is accomplished by complete distillation of the pyroligneous acid, leaving the tar behind in the still. A copper still equipped with closed steam coils is commonly used for this operation, although triple effect evaporators are sometimes used. Since it is simply the separation of a volatile from a non-volatile liquid no special precautions are required. A small amount of oil distils with the water and this is separated before the next operation. The residue of tar is allowed to accumulate in the still for several days and then it is given a steam distillation, like the settled tar, either in the copper still or after removal to the wooden tar still.

The distilled tar-free pyroligneous acid to which is added the water distillate from the tar still is now ready for neutralization with lime. A thick milk of lime is used for the neutralization and the operation is carried out in a covered wooden tub provided with a stirring apparatus. The neutral point is usually determined by the color change in the solution itself which becomes very much darker as the neutral point is reached. In fact, the color is so dark that the use of outside indicators is difficult. A dark wine-color is the common neutral point and this must be attained with considerable accuracy to avoid difficulties in the future evaporation of the acetate solution. During the neutralization an insoluble sludge is formed which settles partly in the neutralizing tub and partly in wooden tanks provided for the storage of the neutralized liquor. The sludge must be occasionally removed from the neutralizing tub which should be designed for accomplishing this readily. The wet sludge retains a considerable amount of acetate liquor and is frequently washed or filtered in a filter press for its recovery.

The neutralized settled solution contains the acetic acid in non-volatile form and the alcohol and other volatile products can be separated from the acid by distillation. Since the solution is now neutral an iron still, commonly called the "lime-lee" still, can be used for this distillation. The lime-lee still is provided with a closed steam coil of copper and no direct steam is used in this operation. The distillation is carried on until the gravity of the distillate is unity showing that all the alcohol has been removed. A small amount of oil also collects with the distillate from this operation and should be separated before the next distillation. The residue in the still is called the acetate liquor and the distillate, the alcohol liquor.

The acetate liquor is commonly evaporated in shallow, steam-jacketed iron pans although single or multiple effect evaporators are frequently used. In the iron pans the first separation of the solid acetate of lime should take place on the surface of the liquor, since if it starts on the bottom of the pan a hard dense deposit forms which reduces the effective heating surface and is very difficult to remove. Starting on the surface the separation of the solid acetate proceeds downward, the steam escaping through small craters in the crust. The

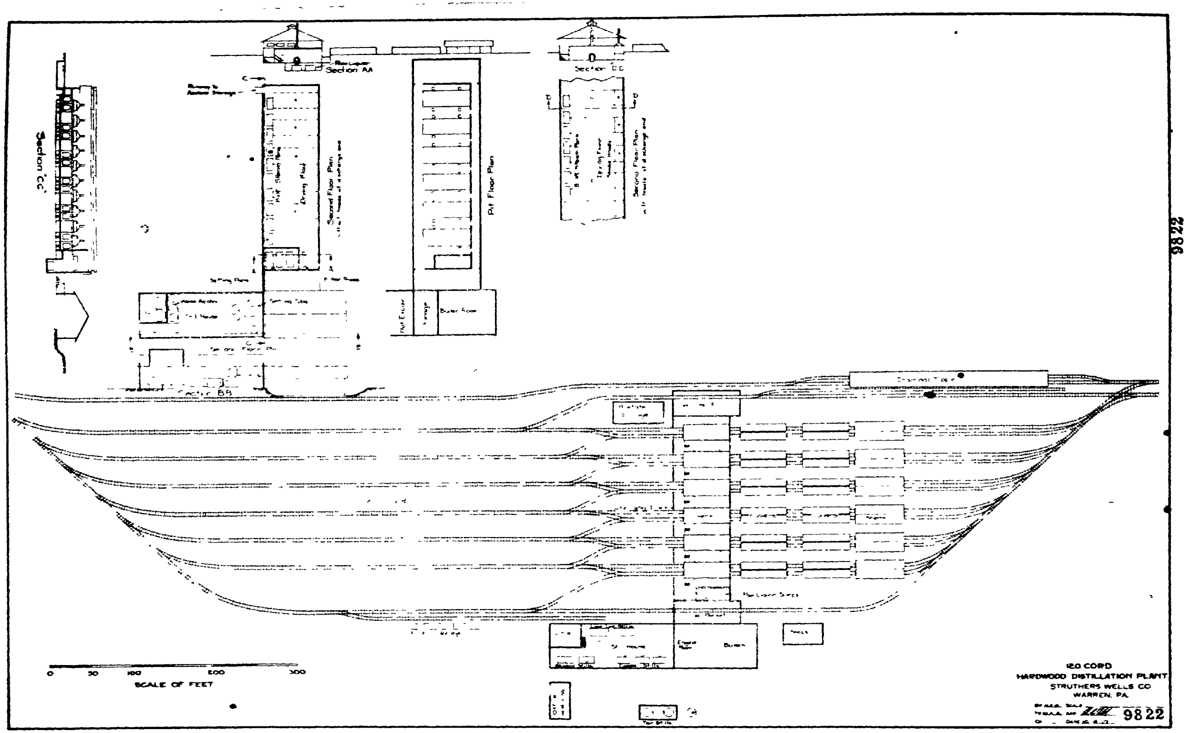

Fig. 4.—Layout of Hardwood Distillation Plant.

evaporation is stopped when the mass has reached the consistency of a thick mud and the rest of the drying takes place elsewhere. For the final drying of the acetate drying floors are provided on top of the ovens where the heat of the flue gases can be used. The acetate mud is spread in a thin layer on the floor and frequently raked to uncover the wet acetate as the top surface dries. The drying acetate is sometimes rolled with a light roller to prevent the formation of too large lumps. The acetate is not decomposed by any temperature likely to be reached on the floor and no special precaution needs to be taken. This is the last operation for the preparation of the finished acetate of lime and when dry it is bagged for shipment.

When multiple effect evaporators are used for evaporating the acetate liquor another method for drying is introduced. The evaporators carry the concentration almost to the point where separation of the solid acetate begins and then the solution is run to a shallow pan into which dips a slowly revolving steam-heated cylinder. The cylinder is provided with automatic scrapers which remove the deposit at proper intervals. Usually the speed of the cylinder, the steam heat and the scraping are coordinated so that the material scraped off has been dried to a consistency of a thick mud. The mud drops to a V-shaped trough in which it is picked up on an endless wire belt. The belt passes through heated chambers where the drying is completed and the dried acetate is removed from the belt by the belt running over rolls which change the direction at sharp angles and by an automatic shaking or beating device. This method of drying is very efficient in the way of saving labor costs, since the acetate is dried and delivered to the storage hoppers without being touched by hand.

The alcohol liquor distilled from the lime-lee still is concentrated to a crude wood alcohol of about 82 per cent strength as determined by the gravity. This concentration can not be reached by a single distillation from an ordinary still without some kind of fractionating column. For a long time the column commonly used was the "Burcey pan," a special type of still head used practically entirely by the hardwood distillation plants. Many other types of columns are now used more in line with modern fractional distillation apparatus. The distillation is controlled by the gravity of the distillate and if the apparatus is not efficient enough to produce the required strength of alcohol in one operation the last part of the distillate is kept separate and returned to the alcohol liquor tank for further treatment. The distillation is stopped when the gravity of the distillate shows no more alcohol distilling and the residue is run to waste. A small amount of oil distils with the alcohol and is separated before further refining.

When evaporators and roll dryers are used for preparing the acetate, the lime-lee still is usually cut out and a continuous column still substituted which is able to prepare a concentrated alcohol direct

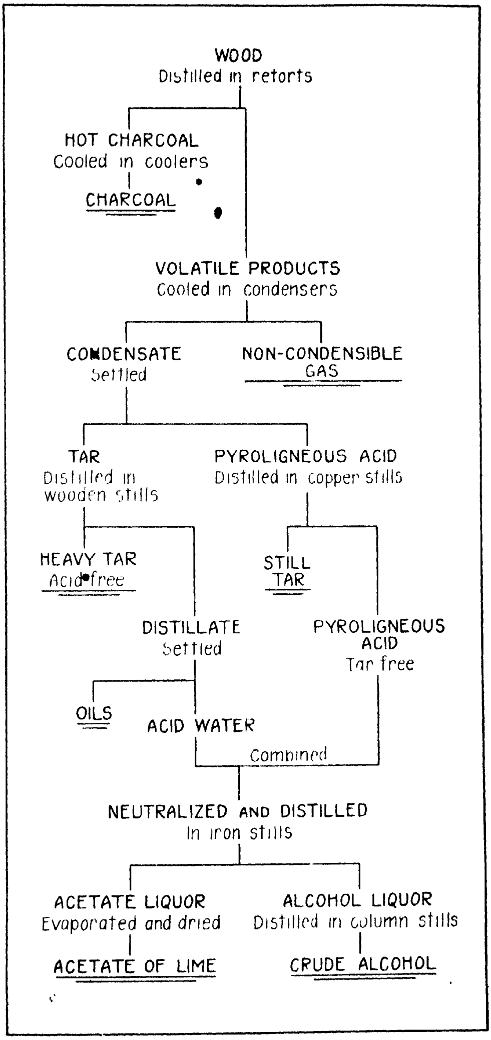

FIG. 5.—Flow Sheet of Hardwood Distillation Process.

from the neutralized pyroligneous acid. This results in a considerable saving, since both the lime-lee and the alcohol still operations are replaced by a single distillation and a larger proportion of acetate liquor is left to be evaporated in the efficient multiple effect evaporators.

In most wood distillation plants the refining of the wood alcohol is carried no further than the preparation of this concentrated crude with no attempt to separate a commercial grade of wood alcohol. The crude is shipped to central refineries where with the advantage of larger scale operation the complicated refining process can be more readily carried out. Some of the larger plants or groups of plants, however, do their own refining. The apparatus and the methods used and the products obtained are so variable that no typical process can be described, but the general principle involved is the separation by fractional distillation of three fractions besides the water. These are in order of boiling points (1) the "methyl acetone" fraction with lowest boiling point, (2) the middle fraction of refined wood alcohol and (3) the highest boiling fraction containing the allyl alcohol. Small amounts of oils soluble in alcohol but not in water are present in the crude alcohol and frequently these are more readily removed from certain fractions by diluting greatly with water, separating the oils, and redistilling the water solution. The only chemical treatments used are simple washings with caustic soda and with sulphuric acid to remove certain impurities but not to help in the separation of the final products. The grade of the alcohol obtained will depend on the efficiency of the apparatus and on the amount and composition of the methyl acetone fraction. With the same conditions otherwise the more "methyl acetone" obtained the higher will be the grade of the alcohol, that is, the less acetone it will contain. The production of a wood alcohol with as little as 0.1 per cent acetone is a difficult operation.

Yields of Products

The yields vary with the quality of the wood and with the care taken in the process so that it is difficult to determine the average. There are also a few kiln plants still in operation, so that the average of all plants is lower than for oven and retort plants only. Census Report for 1919 shows average yields of 142 pounds of acetate of lime, 7.7 gallons of crude wood alcohol and 39 bushels of charcoal per cord. It is believed, however, that there must be some mistake in these figures and that 180 pounds of acetate, 10 gallons of crude wood alcohol and 48 bushels of charcoal per cord of wood is a better average. The Michigan and Wisconsin plants will commonly get less acetate than this and the New York and Pennsylvania plants more, although the wood seems to be very much the same and the apparatus and methods identical. Some plants get over 200 pounds of acetate and 12 gallons of crude alcohol per cord.

New Processes

There are several new processes of wood distillation which have been given some publicity but which are still in the experimental or development stage[1] so that they can not be classed with the commercial processes and details in regard to the process and yields can not be given. They are, however, promising enough from a commercial standpoint or interesting enough from a technical standpoint so that they should be mentioned and briefly discussed.

It happens that all these new processes are designed for the distillation of sawdust or small chips. The advantages of this sort of material are (1) that it may be obtained cheaper than cordwood, (2) that it can be more rapidly and efficiently dried, and (3) that it can be handled by a continuous process. There are, however, many disadvantages in using sawdust or chips. In the first place, wood itself is a good non-conductor of heat and sawdust is even better in this respect, since a mass of sawdust contains many closed air spaces which are still better non-conductors. A stationary mass of sawdust is, therefore, very difficult to distill, since it is almost impossible for the heat required to pass through to the center of the mass. It is necessary, therefore, that the sawdust be stirred either by a rotating retort or by some kind of agitation within the retort. This immediately introduces other complications. Either a stirrer or a rotating retort requires moving parts which must be joined gas-tight to the stationary parts of the retort, and at the temperatures of destructive distillation this is not a simple problem. The agitation of the mass also stirs up a great deal of fine charcoal dust, which tends to be carried out of the retort with the vapors and to clog the condensers. If the process is to be continuous, it is also necessary to introduce the sawdust without introducing too much air and without allowing any of the products of the distillation to escape. The charcoal must also be removed through some kind of a gas-tight seal. The cooling of large quantities of finely divided charcoal is also a difficult problem and this, together with the marketing of large quantities of such a product, again adds to the difficulties of sawdust distillation.

The Briquetting Process

The American Wood Reduction Co. avoided many of the problems in connection with sawdust distillation by making the sawdust into a solid block of wood before distillation. In other words, the sawdust or very small-sized wood was briquetted and distilled in the form of briquets. When sufficient pressure is applied to wood a very solid briquet can be formed without the use of any binding material. These briquets, however, when made of hardwood, tend to fall to pieces during destructive distillation; consequently the benefits of briquetting would be largely lost. It was found, however, that, if these sawdust briquets could be subjected to slight mechanical pressure during the distillation, they remained in one piece and fairly firm, regularly shaped pieces of charcoal could be made by this method.

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[1] Two of these processes have been put in operation in commercial sized plants since this was written.

The process finally developed by this company included the conversion of the waste wood in the form of sawdust or small chips into 4-in. briquets, which were loaded from an automatic loader into retorts, consisting of a series of horizontal tubes 20 ft. long and with an inside diameter slightly greater than that of the briquets. Each of these tubes was provided with a piston, by means of which a small pressure of 8 or 10 lbs. per sq. in. could be exerted continuously against the column of briquets during the distillation. On account of the small diameter of the tubes, each of which really acted as a single retort, the complete distillation could be finished in about three hours, and the temperature control was good enough so that unusually high yields were obtained. The cost of preparing the wood for distillation and the rather complicated and small-capacity apparatus was, therefore, compensated by the high yields and short length of time in the retort. A plant to use this process was under construction during 1918, but was never put into operation, and the process never had a trial on a commercial scale.

The Sawtelle Process

The Sawtelle process also avoided some of the usual complications of sawdust distillation by a combination of the distillation of the wood and the manufacture of producer gas from the charcoal. This was accomplished by using an updraft gas producer with wood as fuel. The wood in the form of sawdust and fine chips forms a cone-shaped pile in the gas producer, the upper part of which is wood in the drying stage, the next layer wood in the stage of destructive distillation, and the lower layers charcoal in the process of manufacture into producer gas. The heat required for distilling and drying is furnished by the hot gas. Since charcoal is not a product of this process, the difficulties with charcoal dust and with cooling the finely divided charcoal are not encountered. This process has operated successfully from the mechanical standpoint in a small commercial unit producer, but accurate yield figures could not be obtained on account of the lack of a gas scrubber. This process produces probably 8

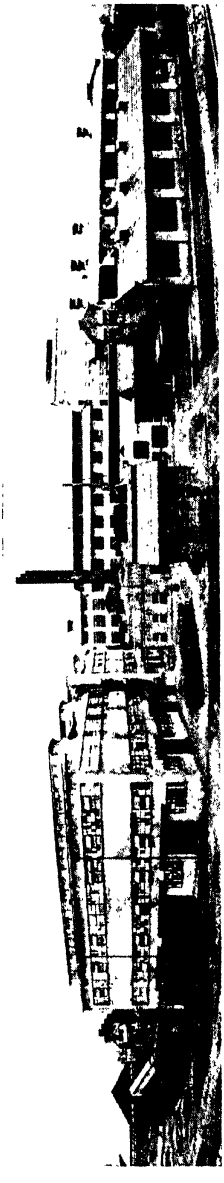

Fig. 6.—Stafford Process Plant.

to 10 times as much gas as the ordinary process and the losses in the unscrubbed gas are, therefore, very high, especially the loss of alcohol. With the use of gas scrubbers there seems to be no reason, however, why this method should not give the maximum yields, since the process is a continuous one and the temperature can readily be controlled. In localities where there is a demand for the producer gas obtained, this process should be very promising, but under present conditions the presence of large quantities of hardwood waste in localities where there is also a demand for power is uncommon.

The Stafford Process

This process was developed with the idea of utilizing fully the exothermic reaction of wood distillation. The process and apparatus is of the simplest, consisting merely of a large, well-insulated chamber into which the dry, warm wood is introduced continuously. The heat of decomposition of the wood is sufficient to bring an equal quantity of dry, warm wood to the distillation point; and the process is, therefore, continuous without the addition of heat from the outside. A thick layer of charcoal is kept in the bottom of the retort and partly cooled charcoal can be withdrawn continuously or at intervals. This process requires no moving parts inside the retort since the heat interchange between incoming wood and the hot vapors and hot charcoal in the retort is rapid enough without any stirring. A large plant using this process is now in commercial operation but no details of the results are available. There seems to be no reason why this process should not obtain maximum yields.

The Seaman Process

The Seaman process was developed and demonstrated in a commercial-sized unit

TABLE 1.

HARDWOODS CONSUMED IN DISTILLATION, BY STATES: 1919.

State	Number of establishments	QUANTITY		COST	
		Cords	Per cent distribution	Total	Average per cord
United States	87	1,186,477	100.0	* $7,965,069	$6.71
Michigan	15	648,910	54.7	4,307,797	6.64
Pennsylvania	42	281,320	23.7	1,882,795	6.69
New York	20	104,493	8.8	747,882	7.16
Wisconsin	3	60,544	5.1	519,131	8.57
All other states. . .	† 7	91,210	7.7	* 507,464	5.56

* Includes one establishment engaged in wood distillation, but primarily operating a blast furnace.

† Includes establishments distributed as follows: Alabama, 1; Connecticut, 1; Kentucky, 1; Mississippi, 1, Missouri, 1, Tennessee, 1, and West Virginia, 1.

several years ago. The apparatus consisted of a rotating inclined retort about 30 ft. long by 3 ft. in diameter. The hot, dry sawdust was charged at the upper end and the charcoal was removed continuously from the lower end. The ingenious devices[2] for introducing the sawdust without introducing air and for removing the charcoal without allowing the escape of gas were found to work very satisfactorily on this demonstration retort. The yield of acetic acid obtained in this apparatus was unusually high, but for some unknown reason the alcohol yields were somewhat low. A commercial plant to use this process was ready for operation early in 1918, but many difficulties were encountered, especially the plugging of the condensers by charcoal dust which was carried over from the retorts. It is reported that these

TABLE 2.

QUANTITY OF PRODUCTS FROM HARDWOOD DISTILLATION: 1919.

Kind	Quantity
Crude wood alcohol . . . . gallons	* 9,103,996
Acetate of lime.. .. .. pounds	168,956,432
Charcoal .... bushels	46,354,342
Tar .... gallons	552,124
Tar oils .... gallons	222,398
Wood creosote .... pounds	945,605

* Includes a small amount of wood alcohol manufactured from softwoods.

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[2] U. S Pat. No. 1,236,885.

difficulties have now been overcome and that several of the retorts are now operating continuously and commercially.

The Whittaker-Pritchard Process

In this process the heating medium is a current of hot gas which circulates from the heater to the distillation chamber to the condenser and then to the heater again. In this way the difficulty of heating finely divided material without stirring is avoided. This process has been used successfully for the destructive distillation of other materials than wood but it has only been suggested as a wood distillation process and even experimental results have not been reported.

Statistics

The latest statistics on hardwood distillation are given in Tables 1, 2 and 3, taken from the Bureau of Census report, "Forest Products: 1919." Table 1 shows that this industry has made a start in the South, although for many years it was confined entirely to the northern hardwood regions. Since 1919 other plants have been put into operation in Tennessee and West Virginia, so that the southern representation is even greater than shown in the table. The New York and Pennsylvania plants are in two groups, one in northwestern Pennsylvania around Bradford with two plants just across the line in New York, and the other in northeastern Pennsylvania and contiguous parts of New York. The Michigan plants are in the north peninsula and the northern part of the south peninsula. The Wisconsin plants are in the most northern parts of the state.

TABLE 3.

EQUIPMENT USED IN HARDWOOD DISTILLATION.

State	RETORTS		OVENS		KILNS		Aggregate capacity (cords)
	Number	Total capacity (cords)	Number	Total capacity (cords)	Number	Total capacity (cords)	
Michigan	160	1,102	20	180	130	8,200	9,482
New York	188	279	47	386	...	....	665
Pennsylvania	214	686	159	1,312	12	120	2,118
Wisconsin	10	82	...	....	25	1,750	1,832
All other states*	56	527	6	60	...	....	587
Total	628	2,676	232	1,936	167	10,070	14,684

* Includes Alabama, Connecticut, Kentucky, Mississippi, Missouri, Tennessee, and West Virginia.

Table 3 gives the total capacity in cords of the retorts, ovens and kilns. These capacity figures are not in cords per day, however, but in actual holding capacity of the apparatus regardless of how long it might take to distil a charge of wood. This method of reporting makes the kilns seem more important than they really are, since the actual daily capacity of kiln plants in operation in 1919 was probably not more than 400-500 cords. On this basis the rated capacity of the plants in operation in 1919 was about 5,000 cords per day and figuring on 300 working days per year the plants were producing at about 79 per cent of rated capacity.

There is also a mistake in the classification into retorts and ovens in Table 3, since there are no retort plants in Michigan or Wisconsin, and since the capacity of the "retorts" as given for these states and for "all other states" is seen to be about the same as that of the ovens, while the cylindrical horizontal retorts hold only about 1 cord each. This mistake is probably due to the fact that in the localities to which the industry has more recently spread the old fashioned cylindrical retort plant has never been built and the operators are likely to call their ovens "retorts," since there are no real retorts in their vicinity to furnish the distinction between the two terms. In New York and Pennsylvania, where there are a few retort plants left and the memory of many others, the distinction between "retort" and "oven" is more likely to be properly made.

The War Industries Board Price Bulletin No. 51 gives an estimate of production for the year 1917 which shows the effect of the war demands for these products. Acetate of lime production was estimated at 200,000,000 pounds for 1917 and refined wood alcohol and methyl acetate at 8,000,000 and 1,400,000 gallons, respectively. The production during 1918 was probably even greater than this.

The United States is by far the largest producer of wood distillation products. For comparative purposes the estimated figures for 1914 are given for the United States, Germany-Austria and Canada, the three largest producers:

	Acetate Tons	Wood alcohol Gals.	Wood used Cords
United States	80,000	9,000,000	1,000,000
Germany-Austria	25,000	2,800,000	300,000
Canada	8,500	950,000	110,000

It is not known in what countries the production listed under Germany-Austria is now located but it is believed that most of the crude products are manufactured in Czecho-Slovakia.

Aside from these countries, Sweden, England, Japan, and France are known to have small wood distillation industries but accurate statistics are available only for Sweden. In 1917 Sweden produced alcohol and acetate equivalent to the rated capacity of one 50-cord plant using American hardwoods. Sweden has several well equipped wood distillation plants and the explanation of the small output is that hardwoods are not abundant and resinous wood is the raw material commonly used resulting in low yields of wood alcohol and acetate. In 1915 Japan had developed an industry which gave an output equivalent to about one 50-cord plant. France has had a small industry for some time. It is reported that Argentina has started a small industry and one plant has recently begun operation in India.

Importance of Wood Distillation Products

Before 1916 the products made by wood distillation were not obtainable commercially from any other source except acetic acid in the form of vinegar and this was not a competing product, since it was used only in food products and acetic acid from wood distillation was not used in this way. The great demands for acetic acid and acetone during the war, however, led to the development on a commercial scale of several new processes for making these products. Of these new processes two have continued in operation since the war and may become serious competitors of hardwood distillation. One is the production of acetic acid synthetically from acetylene and the other is a fermentation process for obtaining acetone direct from starch.

Charcoal

Charcoal has been known and used as a fuel since prehistoric times, but at present it has only special fuel uses. Probably the largest single use of this kind is in blast furnaces for the manufacture of charcoal iron. Many wood distillation plants are built in connection with blast furnaces, and their entire output of charcoal is used for this purpose. It is also used largely as a special domestic fuel, and considerable quantities are still employed in the manufacture of black powder. Charcoal has also a large number of miscellaneous uses, such as in stock and poultry foods, in case-hardening compounds, and as a deodorizer and heat insulator.

Acetic Acid

Acetic acid has a wide use in the chemical industry in the preparation of various inorganic acetates such as lead, copper, and sodium acetates, and in the preparation of white-lead pigment. It is used widely in the organic chemical industry, especially in the preparation of cellulose acetate for films, laquers, plastics and artificial silk; and in the preparation of various organic acetates, such as methyl, ethyl and amyl acetates which are used as solvents. It enters in the manufacture of various synthetic organic chemicals such as indigo, salvarsan and acetyl-salicylic acid. It has also several miscellaneous uses, as in textile plants in the dyeing process, in laundries, in tanning, and in the manufacture of insecticides, soaps, toilet articles, and chrome yellow. It is also used on rubber plantations for coagulating the latex.

Fig. 7.—Retort House, Coolers, and Charcoal Sheds.

Acetone

Acetone is used largely as a solvent and for certain purposes of this kind it seems to be almost indispensable. This is especially the case with certain cellulose acetate films and lacquers, which require a large proportion of acetone in the solvent for obtaining the best results. The smokeless powder used by the British Government is generally made with acetone as a solvent. Large quantities of acetone have also been used as a solvent for acetylene in portable lighting and welding outfits. About the only chemical use of acetone is in the manufacture of chloroform and iodoform.

Wood Alcohol

Wood alcohol has a large number of uses for which there seems to be no substitute possible. Formerly the largest use of wood alcohol in this country was as a solvent in the manufacture of varnishes and lacquers, especially those containing shellac. This use has, however, declined very rapidly of late, and only small quantities of wood alcohol are now being used for this purpose. The uses in which wood alcohol enters into chemical reaction with other materials have been rapidly growing and about the only important remaining use of wood alcohol as a solvent is in connection with the manufacture of moving-picture films. Its main chemical use is probably in the manufacture of formaldehyde, as it is the only raw material from which formaldehyde has been produced commercially. Formaldehyde is a standard disinfectant for general use in hospitals and sick rooms. An even more important use for formaldehyde, however, is found in the eradication of various fungus diseases which attack seed grains. The Department of Agriculture has recommended the use of formaldehyde treatment for potatoes and for many grains, in order to prevent these diseases and increase the yields of the products. Formaldehyde is also the base used in the rapidly increasing production of synthetic resins, such as Bakelite and Redmanol. Wood alcohol is now used in the preparation of certain dyes which require the presence of the methyl group. Methyl acetate and methyl salicylate, or artificial oil of wintergreen, and other similar methyl esters require wood alcohol in their production.

Methyl Acetone

Methyl acetone, which is a mixture of wood alcohol, acetone, methyl acetate and other impurities in small quantities, is obtained during the refining of wood alcohol. This material naturally varies in composition as produced at different refining plants, but it has the same general uses in all cases—namely, as a solvent. It has solvent properties very similar to acetone and in general superior to those of pure wood alcohol. Its special use, however, is in the denaturing of ethyl alcohol.

Wood Tar

Wood tar has not yet become an important product of wood distillation, although there has been considerable development along this line within the last few years. Flotation oils, solvent oils, heavy tar oils for paints, stains, preservatives and insulating pitch are some of the important products obtained from wood tar. One important product for which wood tar is the only raw material is the medicinal beechwood creosote which has been manufactured to a considerable extent in this country since 1915.

Chapter II.

Wood, the Raw Material.

The three main constituents existing separately in woods are the wood fiber, the extractives and water. The wood fiber is a ligno-cellulose which, as will be seen later, does not differ markedly in different species except between the two main divisions of hardwoods (deciduous woods, angiosperms) and softwoods (conifers, evergreens, resinous woods, gymnosperms). The extractives are the substances soluble in neutral solvents and may consist of gums, resins, tannins, volatile oils, bitter principles, carbohydrates or coloring matter. Most of the striking differences in woods, such as color and odor, are due to the extractives alone, but differences in specific gravity may be due either to extractives or to the physical structure of the fibres. Water is always a natural constituent of the wood and is present in most wood even after it has been dried by any ordinary method. It is not an important constituent chemically except that it is very variable and the amount of it present must be known in order to determine the exact amount of dry wood in a known amount of wet wood. This may seem self evident but it is a point frequently overlooked in both industrial and experimental work with wood.

The dividing line between these main constituents is sometimes hard to distinguish, as for instance whether a certain gum is an easily hydrolized constituent of the ligno cellulose or whether it occurs as an extractive separate from the ligno-cellulose. The dividing line between water and wood fiber is usually drawn at 105° C., although at higher temperatures small amounts of water may be driven off which may not be strictly water of constitution.

Wood Analysis and Composition

Methods of analysis have been developed for wood which determine quantitatively the various constituents or groups of constituents existing separately in the wood and also the various chemical groups or radicals which exist in the ligno-cellulose aggregate. Commonly the constituents thus determined are not all distinct and separate so that the results are not additive but Dore[1] has succeeded in arranging the percentage results of certain determinations so that they add to approximately 100 per cent in the case of softwoods. Some of the "constituents" are very indefinite in composition and some are merely chemical constants of the ligno-cellulose or of the total wood, but if the methods by which they are determined are specified in detail the analytical results can be duplicated with fair accuracy. Very wide variations can be obtained by slight modification of the method of analysis or of the method of preparing the sample, so that results by different analysts usually can not be compared. One analyst may determine that the cellulose in a certain species of wood is 65 per cent and another may find 55 per cent. This may not be due to faulty methods or careless work but to the fact that the two analysts have different definitions of "cellulose." There is also a variation in composition of wood from different trees of the same species and from different parts of the same tree, so that the average composition of the wood of one species can not be based on one or two samples unless these are composite samples carefully selected.

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[1] *Jour. Ind. Eng. Chem. 11*, 556 (1919)

It was with these facts in view that a series of chemical analyses of wood was started by the Forest Products Laboratory some time ago.[2] It was decided that the results should be as truly comparative for the different species as was possible with a reasonable number of analyses and, therefore, samples were selected with care and the same methods of analysis, with slight modification, were used throughout. Table 4 gives the main results of this series of analyses.[3] The results of other investigators are not mentioned since they would not be comparable with these and no other so comprehensive series of wood analyses exists.

The hot and cold water soluble and the ether soluble determinations represent most of the extractives, the first two including the gums and tannins, the last including the resins and volatile oils. The 1 per cent sodium hydroxide soluble includes most of the extractives as well as part of the pentosans and certain ill-defined portions of the lignin.

The figure for "acetic acid by hydrolysis" is the percentage of total volatile acid (computed as acetic acid) obtained by boiling the wood with 2½ per cent sulphuric acid. This total volatile acid usually contains a small proportion of formic acid.

The methoxyl groups ($CH_3O—$) are determined by treating the wood with hydriodic acid and determining the amount of methyl iodide formed.

The pentosans are determined from the amount of furfural formed on boiling the wood with 12 per cent hydrochloric acid. Sometimes

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[2] Schorger, *Jour. Ind. Eng. Chem. 9*, 556 and 561 (1917).

[3] The work started by Schorger has been continued by Mahood and Cable, *Jour. Ind. Eng. Chem. 16*, 3752 (1922), and by Ritter and Fleck, *Jour. Ind. Eng. Chem. 16*, 4337 (1922).

TABLE 4.

ANALYSIS OF WOODS.

Results in percentage of oven-dry (105° C) samples.

Species	Ash	Solubility in				Acetic acid	Methoxy	Pentosan	Cellulose	Lignin	In cellulose			
		Cold water	Hot water	Ether	1 per cent NaOH						Pentosan	Alpha cellulose	Beta cellulose	Gamma cellulose
Western yellow pine..... (Pinus ponderosa)	0.46	4.09	5.05	8.52	20.30	1.09	4.49	7.35	57.41	26.65	6.82	62.10	10.56	30.13
Yellow cedar ... ... (Chamæcyparis nootkatensis)	0.43	2.47	3.11	2.55	13.41	1.50	5.25	7.87	53.86	31.32	7.30	62.68	11.06	26.25
Incense cedar .... (Libocedrus decurrens)	0.34	3.64	5.38	4.31	17.60	0.01	6.24	10.65	41.60	37.68	9.08	46.92	11.67	41.06
Redwood (heartwood).. (Sequoia sempervirens)	0.21	7.36	9.80	1.07	20.00	1.08	5.21	7.80	48.45	34.21	7.40	78.81	2.95	18.24
Western white pine..... (Pinus monticola)	0.20	3.16	4.49	4.26	14.78	1.03	4.56	6.07	5[illegible].71	26.44	5.33	64.61	16.32	19.06
Longleaf pine ... . (Pinus palustris)	0.37	6.20	7.15	6.32	22.36	0.76	5.05	7.46	58.48	.....	7.71	.....	.....	.....
Douglas fir .... (Pseudotsuga taxifolia)	0.38	3.54	6.50	1.02	16.11	1.04	4.05	6.02	61.47	...	5.34	.....	.....	.....
Western larch . .. . (Larix occidentalis)	0.23	10.01	12.59	0.81	22.14	0.71	5.03	10.80	57.80	....	8.94	.....	.....	.....
White spruce . ... (Picea canadensis)	0.31	1.12	2.14	1.36	11.57	1.59	5.30	10.39	61.85	...	9.63	.....	...	.....
Tanbark oak . .. (Quercus densiflora)	0.83	4.10	5.66	0.80	23.06	5.23	5.74	10.59	58.03	24.85	22.82	56.77	19.92	23.03
Mesquite . . . ... (Prosopis juliflora)	0.54	1.02	15.00	2.30	28.52	2.03	5.55	13.96	45.48	30.47	17.75	76.48	2.35	21.17
Balsa ... . (Ochrona lagopus)	2.12	1.77	2.79	1.23	20.37	5.80	5.6[illegible]	17.65	54.15	26.5[illegible]	19.99	75.64	0.27	24.08
Hickory (shellbark) ... (Hicoria ovata)	0.69	4.78	5.57	0.63	19.04	2.51	5.[illegible]3	18.82	56.22	23.44	21.8[illegible]	76.32	2.82	20.35
Eucalyptus (Eucalyptus globulus)	0.23	4.67	6.98	0.56	18.57	1.85	6.73	19.91	57.02	25.27	20.06	68.86	0.70	31.10
Basswood .... (Tilia americana)	0.86	2.12	4.07	1.96	23.76	5.79	6.00	19.93	61.24	.....	24.[illegible]8	.....	.....	.....
Yellow birch .... (Betula lutea)	0.52	2.67	3.97	0.60	19.85	4.30	6.07	24.63	61.31	.....	28.30	.....	.....	.....
Sugar maple .... (Acer saccharum)	0.44	2.65	4.35	0.25	17.64	4.46	7.25	21.71	60.78	.....	24.48	.....	.....	.....

methyl pentosans are also determined, but these seem to have little significance and are not included in Table 4.

Cellulose is such a poorly defined material that there is much difference of opinion as to what wood residue should be called "cellulose" and there is a tendency to write the word in quotations so as not to convey the impression that a certain definite compound is meant, but in this discussion cellulose is fairly closely defined by the method of separating it. By treating the wood with chlorine gas, a water solution of sulphur dioxide, and hot water in this order repeatedly until all color has been removed, a residue is obtained which is the "cellulose" of this discussion. This is the "Cross and Bevan" cellulose which has been the basis of the analysis of many cellulosic materials and the results of its determination can be duplicated with accuracy.[4] That this cellulose is not of the same composition when prepared from different woods is shown, however, by the variation in the values for "pentosan in cellulose" and for the alpha, beta and gamma cellulose.

FIG. 8 Loading the Buggies with Wood

The lignin is obtained as a residue on treating the wood with 70 per cent sulphuric acid. The cellulose as separated by the method described above is subsequently divided into three kinds of cellulose, the alpha cellulose being insoluble in 17.5 per cent sodium hydroxide, the beta being soluble but reprecipitated by acetic acid and the gamma being soluble and not reprecipitated.

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[4] See Schorger and Mahood and Cable for details. *Loc. cit.*

It should be noted here that each of these determinations except those under the heading "In cellulose" is made on a separate sample of wood and that many of the constituents overlap. For instance, most of the cold water soluble is also determined in the hot water soluble, most of the cold water, hot water, and ether soluble in the alkali soluble, most of the methoxyl in the lignin, and part of the pentosans in the alkali soluble.

Aside from the results shown in Table 4 there are a few series of determinations of single constituents of woods which should be mentioned here. Methoxyl determinations on a large number of woods have been made by Benedikt and Bamberger.[5] In comparing their figures with those in Table 4 it should be noted that they express their results in terms of "methyl numbers" instead of methoxyl and that their figures should, therefore, be multiplied by 31/150 for proper comparison. They suggest this methoxyl determination as a measure of the "lignification" of the wood, but Table 4 shows that there is no close relation between the amounts of methoxyl and lignin.

The nitrogen content of several species of wood has been determined by Koenig and Becker[6] and their results are shown in Table 5.

TABLE 5.

NITROGEN CONTENT OF WOOD.

	Protein N × 6.25	Nitrogen
	Per cent	Per cent
Fir No. 1	1.21	0.19
Fir No. 2	1.21	0.19
Pine	1.27	0.20
Birch No. 1	1.29	0.21
Birch No. 2	2.29	0.36
Poplar No. 1	1.39	0.22
Poplar No. 2	1.14	0.18
Beech	1.58	0.25
Ash	1.30	0.21
Willow	1.17	0.19
Alder	1.89	0.30

Many other determinations of various constants and constituents of these species are also reported in this article, but they will not be given here, since they are not closely comparable with the results given in Table 4. One point of special interest is that they report the lignin content of conifers to be regularly higher than that of hardwoods.

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[5] Monatsh, *11*, 260 (1890).

[6] *Papier-Fabrikant* *37*, 981 (1919).

The content and composition of the ash in various species shown in Table 6 are taken from White's work.[7]

The variation in chemical composition between heartwood and sapwood has not been systematically studied, but in general the extractives are higher in the heartwood, this being surely the case with resins and coloring matter.

TABLE 6.

ANALYSES OF WOOD ASHES.

Species	Ash content of dry wood	Potash in ash (K_2O)
Hardwoods	Per cent	Per cent
Hickory	0.81	18.93
Red oak	0.94	16.41
White oak	0.41	29.90
Post oak	1.21	15.46
Dogwood	1.05	20.03
Ash	0.47	34.74
Chestnut	0.20	13.33
Sycamore	1.10	18.24
Magnolia	0.67	19.54
Average for hardwoods	0.76	20.28
Softwoods		
Pinus palustris	0.54	15.35
Pinus mitis	0.38	12.97
Picea nigra	0.32	10.43
Average for softwoods	0.41	12.91

Variation in Composition of Species

The main variations in composition are between the hardwoods and the softwoods. The hardwoods are generally higher in the amount of acid by hydrolysis, methoxyl groups, pentosans, and pentosans in cellulose. The ash and the potash content of the ash are also higher in the hardwoods. Contrary to the general opinion the cellulose is not generally higher in softwoods and the lignin is not generally higher in hardwoods.

The high ether soluble in longleaf pine and Western yellow pine is due to the high resin content of the wood from these species. The high water soluble in Western larch is due to a gum, galactan, which occurs in unusually large quantities in this species.[8] The composition of the material which furnishes the high water soluble value for mesquite is not known. The action of 1 per cent sodium hydroxide is greater on hardwoods than on softwoods, the average of hardwoods from Table 4 being 21.5 per cent and the softwoods 17.6 per cent. This difference is more marked if we exclude the woods which have high water soluble or ether soluble and include only those in which the action of the alkali is mainly on the ligno-cellulose (probably on the pentosans). Excluding mesquite from the hardwoods and longleaf pine, Western yellow pine and larch from the softwoods, the average solubilities in alkali of the rest are, respectively, 20.5 per cent and 15 per cent.

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[7] Bull. No. 2 Georgia Experiment Station. Reported by Bateman, *Chem. & Met. Eng.* *21* (1919).

[8] Schorger and Smith. *J. A. C. S.* *8*, 404 (1916).

Another difference between the hardwood and softwood groups which does not show in the table was studied by Schorger[9] who found that all the softwoods contained mannan, some in quantities as high as 7 per cent, while the hardwoods contained none of this substance.

Effect of Composition on Value for Distillation

There are no direct and quantitative relationships known between the composition of a wood and the value for distillation, that is, chemical analysis will not give sufficient information on which to base the probable yields of distillation products. There is, however, an apparent connection between some of the values determined by analysis and the yields of methyl alcohol and acetic acid. It would naturally be expected that the methoxyl groups would be the only source of methyl alcohol and that the yield of this product by destructive distillation would, therefore, bear a relation to the amount of methoxyl in the wood. To a limited extent this is true, but unfortunately only a small and variable part of the methoxyl in the wood forms methyl alcohol on distillation. It has been noted that the hardwoods have generally higher methoxyl values than the softwoods and it is also true that the yields of methyl alcohol are also higher from the hardwoods, but the ratio of methoxyl groups to methyl alcohol is not the same in the two classes of wood, being about 4 for certain hardwoods and about 7 for certain softwoods. There are not enough figures available to show whether these ratios hold for all species, but in the case of maple and birch, which differ in methoxyl content by about 1 per cent, there is a corresponding difference in methyl alcohol yields.

The acetic acid by hydrolysis is higher in hardwoods and the acetic acid by distillation is also higher, but here there is no sort of regularity in the ratios between these values. In fact, it is unlikely that the acetic acid obtained from wood by these two methods comes from the same part of the ligno-cellulose, since cellulose yields little acetic acid by hydrolysis but considerable by distillation. Klason[10] has also shown that birch cellulose yields much more acetic acid on distillation than spruce cellulose.

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[9] The Chemistry of Wood, III. *Jour. Ind. Eng Chem.* 9, 748 (1917).

[10] *Arkiv for Kemi, Min. och Geol*, 1907. *Z. angew Chemie* 25, 1205 (1909)

It is not known just what effect the various extractives may have on the yields of distillation products except in the case of very resinous woods, such as "lightwood" or stumpwood from longleaf pine where the resin is the source of the main valuable distillation products. This will be treated as a special case in another chapter.

It is also unknown what effect the other differences in composition between hardwoods and softwoods have on the products of distillation. The much greater proportion of pentosans in the hardwoods must influence the distillation products in some way, but this effect has never been noticed.

FIG 9.—Charcoal going from First to Second Coolers.

When we have more comparative figures on chemical analyses and yields of distillation products not only from the same species but from the same pieces of wood it will probably be possible to find some closer connection between analyses and yields, but at present the data are too fragmentary. It may be possible sometime to determine the value of a wood for methyl alcohol production from the methoxyl content and even at present the greater value for methoxyl than for the methyl alcohol obtained by distillation is useful in showing the possibility of greater alcohol yields.

Yields from Various Species and Forms

As will be noted in a future section the yields of various products can be varied by the conditions of distillation and, therefore, most of the comparisons of species and forms to be given here will be from one series of tests made under as nearly as possible the same conditions. With the usual variations in the wood from the same species and with the difficulty of controlling the distillation conditions it is not to be expected that one or two test runs will give the average for the species, but only by careful selection of the wood and averaging the results from several runs can satisfactory figures be obtained. Most of the results given here are taken from the Forest Service work on this subject.[11]

The distillations were made in a horizontal, cylindrical retort 15″ in diameter and 36″ long, heated by an oil jacket. The average moisture content of the wood was determined from small blocks cut from selected portions of the charge just before going to the retort and the yields were computed on the dry weight of the wood. The acetic acid yields are the total volatile acid figures determined by distillation and titration of a portion of the pyroligneous acid. This introduces a slight error, since some formic acid is always present. The alcohol yields are determined from the specific gravity after several distillations with excess of sodium hydroxide; they, therefore, include acetone, methyl acetate and other low gravity products which may be present, but the methyl acetate would be mostly hydrolyzed by the treatment and acetone occurs only in small quantities when wood is distilled under these conditions.

Table 7 gives the yields of alcohol and acid from several forms and species. It is seen that the species most commonly used for distillation, beech, birch and maple, are among the highest, while oak, which has only recently been used in large quantities, is lower in both acid and alcohol. Hickory, elm and ash are also high in alcohol yields.

The variation in yields between heartwood and sapwood or heartwood and slabs (sapwood and bark) is variable both in amount and direction. The high acid yield of beech slabs is shown to be due to the sapwood, while the high alcohol yield of maple slabs is due to the bark. Much further work needs to be done to get figures on heartwood, sapwood and bark for the different species.

Similar small scale experiments have recently been made on 46 species of wood from South India, Mysore and Baroda.[12] None of these woods gives yields of both alcohol and acetate as high as the

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[11] Dept Agr. Bulls. 129 and 508, "Yields from the Destructive Distillation of Certain Hardwoods."

[12] Watson and Sudborough. *Jour. Ind Inst Sci.*, Vol 2, Part VII, p. 79 (1918), and Vol. 3, Part IX, p. 281 (1920).

TABLE 7.

Yields of Alcohol and Acid from Various Species and Forms of Wood.

Species	Locality	Wood alcohol 100 per cent					Total acetic acid				
		Heart-wood	Slab-wood	Mean heart and slab	Other forms		Heart-wood	Slab-wood	Mean heart and slab	Other forms	
		Per cent	Per cent	Per cent		P.ct.	Per cent	Per cent	Per cent		P.ct.
Beech	Indiana	1.95	1.79	1.87	Bark Sapwood	1.25 1.97	5.56	6.18	5.87	Bark Sapwood	2.98 6.67
"	Pennsylvania	2.23	2.09	2.16			5.77	6.21	5.99		
Birch	Wisconsin	1.45	1.55	1.54			6.71	6.88	6.80		
"	Pennsylvania	1.62	1.59	1.60			6.19	6.10	6.15		
Maple	Wisconsin	1.94	1.91	1.93	Bark	1.88	5.42	5.11	5.24	Bark	3.15
"	Pennsylvania	1.94	1.78	1.86			5.66	5.44	5.55		
Red Gum	Missouri	1.76	1.73	1.75			5.70	5.23	5.46		
Chestnut	New Jersey	0.90	0.87	0.89	Limbs	0.96	5.50	5.26	5.36	Limbs	6.42
Hickory	Indiana	2.08	....	....			5.05	....	....		
White Oak	"	1.34	1.33	1.33			4.97	4.77	4.87		
" "	Arkansas	1.33	1.46	1.39			4.23	4.35	4.29		
Tupelo	Missouri	1.56	1.86	1.71	Limbs	1.64	4.49	8.19	4.84	Limbs	5.64
White Elm	Pennsylvania	2.12	1.68	1.90			6.39	6.61	6.50		
Slippery Elm	Wisconsin	2.03	1.79	1.91			5.77	5.53	5.65		
Silver Maple	"	1.69	1.77	1.83			6.30	5.31	5.81		
Green, Blue and Yellow Ash	Tennessee Missouri	1.91	1.43	1.67			4.64	4.14	4.39		
Black Ash	Wisconsin	1.79	2.04	1.91			5.65	5.16	5.40		
Green Ash	Missouri	....	....	....	Limbs	2.02	....	....	....	Limbs	4.51
Chestnut Oak	Tennessee	1.22	1.30	1.27			4.88	4.91	4.90		
Tanbark Oak	California	1.72	....	....	Limbs	1.66	6.89	....	....		
Black Oak	"	....	1.53	....			....	6.01	....	Limbs	6.76
Swamp Oak	Louisiana	1.50	1.31	1.40			4.90	5.43	5.16		
Eucalyptus	California	1.33	1.68	1.50			4.58	5.31	4.94		

TABLE 8.

YIELDS OF PYROLIGNEOUS ACID, CHARCOAL AND TAR FROM VARIOUS SPECIES OF WOOD.

	Pyroligneous acid			Charcoal			Tar			Locality
	Heart	Slab	Mean	Heart	Slab	Mean	Heart	Slab	Mean	
Beech	32.3	35.4	33.8	43.1	39.4	41.2	9.7	10.6	10.1	Indiana
"	35.9	35.2	35.5	40.6	42.3	41.4	9.1	10.9	10.0	Penn.
Birch	34.2	34.4	34.3	39.0	38.1	38.5	9.6	8.5	9.0	Wisconsin
"	37.1	33.6	35.3	36.4	38.6	37.0	12.6	10.3	11.4	Penn.
Maple	33.2	31.5	32.4	39.8	44.9	42.3	12.4	9.2	10.8	Wisconsin
"	33.4	34.6	34.0	40.2	37.6	38.9	12.5	12.3	12.4	Penn.
Red Gum	38.2	32.0	35.1	36.8	47.4	42.2	11.7	7.5	9.6	Missouri
Chestnut	36.1	20.4	32.8	47.6	52.9	50.4	4.7	3.7	4.2	New Jersey
Hickory	37.5	....	. .	37.7	....	....	13.0	....	....	Indiana
White Oak	32.7	31.1	31.9	49.5	50.5	50.0	6.3	4.0	5.4	Indiana
" "	35.5	34.4	34.9	42.0	46.2	44.1	9.3	8.7	9.0	Arkansas
Tupelo	35.4	34.9	35.2	45.9	46.1	46.0	11.4	12.1	11.7	Missouri
White Elm	35.6	37.5	36.5	40.0	30.7	39.8	12.1	11.1	11.6	Penn.
Slippery Elm	33.9	31.5	32.7	40.7	44.0	42.4	9.6	7.0	8.3	Wisconsin
Silver Maple	36.8	32.4	34.6	41.2	44.6	42.9	12.1	8.0	10.1	Wisconsin
Green, Blue and Yellow Ash	33.8	28.8	31.3	41.0	45.8	43.4	11.3	7.9	9.6	Tennessee Missouri
Black Ash	35.1	34.1	34.6	38.2	40.5	39.3	11.4	9.1	10.2	Wisconsin
Green Ash	.	.	30.7	....	. .	40.4		. .	10.1	Missouri
Chestnut Oak	35.6	29.8	32.7	39.6	46.9	43.2	10.2	8.8	9.5	Tennessee
Tanbark Oak	37.2	....	...	37.6	...	....	9.0	....	..	California
Black Oak	...	34.0	35.1	....	41.9	40.6	..	10.0	10.2	California
Swamp Oak	31.7	20.8	30.7	46.5	47.4	46.9	7.3	8.9	8.1	Louisiana
Eucalyptus	32.7	34.9	33.8	48.2	44.2	46.2	3.7	8.8	6.3	California

standard American woods, beech, birch and maple. Four species give alcohol yields of more than 2 per cent based on the dry weight of the wood, but the highest acid yield from any of these three is only 4.94 per cent. This is also the highest acid yield from any of the 46 species. The distillations and analyses were carried on in much the same way as those recorded in Table 7 so that the results should be comparable.

Table 8 shows the yields of pyroligneous acid, charcoal and tar from the same distillations recorded in Table 7. These figures are not of so much importance and can not be compared so accurately on account of the fact that they may be made to vary to a certain extent by the maximum temperature to which the charge is carried. For instance, a slightly higher final temperature will certainly decrease the yield of charcoal and possibly increase the yield of tar. The pyroligneous acid figures do not vary widely and seem to have no particular significance, but there is a certain amount of relationship between the tar and charcoal values and those for wood alcohol given in Table 7. This relationship is brought out in Table 9 in which are arranged most [13] of the species of Tables 7 and 8 in order of the alcohol yields. The tar and charcoal figures are seen to arrange themselves in some semblance of order, the tar values decreasing with decreasing alcohol and the charcoal values increasing in the same direction. Especially noticeable are the high charcoal values for the oaks, chestnut and eucalyptus and the low alcohol and tar values for chestnut. It is not known how much significance these figures may have, but it is possible that more accurate and complete determinations would give more regularity in this arrangement and develop more definite conclusions.

TABLE 9.

RELATION BETWEEN YIELDS OF ALCOHOL, TAR AND CHARCOAL.

Species	Alcohol	Total tar	Charcoal
	Per cent	Per cent	Per cent
White Elm	2.12	12.1	40.0
Hickory	2.08	13.0	37.7
Maple	1.94	12.8	40.6
Mixed Ash	1.91	11.3	41.0
Silver Maple	1.89	12.1	41.2
Black Ash	1.79	11.4	40.5
Red Gum	1.76	11.7	38.6
Tupelo	1.56	10.6	44.1
Swamp Oak	1.50	7.3	46.5
White Oak	1.34	7.8	45.7
Eucalyptus	1.33	3.7	48.2
Chestnut Oak	1.20	10.2	46.9
Chestnut	.90	4.6	47.6

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[13] Beech, slippery elm, tanbark oak, and birch are left out, since they do not follow the general rule for the other species.

TABLE 10.

SMALL SCALE DISTILLATIONS BY SENFFT.

		Total distillate	Tar	Acetic acid	Charcoal	Gas
		Per cent	Per cent	Per cent	Per cent	Per cent
Betula alba	a	51.05	5.40	5.63	20.24	19.71
(Birch)	b	42.08	3.24	4.43	21.46	35.56
Fagus sylvatica	a	51.65	5.85	5.21	26.69	21.66
(Beech)	b	41.35	4.90	3.86	21.90	33.75
Quercus robur	a	48.15	3.70	4.08	31.08	17.17
(Oak)	b	45.24	3.20	3.44	27.73	27.03
Pinus abies	a	45.37	4.42	2.73	30.27	24.36
(Fir)	b	51.75	0.77	2.30	24.18	24.07
Pinus larix	a	51.61	0.30	2.00	26.74	21.65
(Larch)	b	43.77	5.58	2.00	24.06	32.17

a = slow distillation.
b = fast distillation.

We have no such complete figures for the alcohol and acid yields from softwoods, but the general rule is that the yields of these products are very much lower, so low in fact that there is not much interest in determining the exact figures. Douglas fir has been shown to give about .69 per cent alcohol and 1.5 per cent acetic acid when distilled in semi-commercial apparatus.[14] The figures in Table 10 taken from Senfft [15] are not comparable with those in the previous tables because they were obtained under different conditions of distillation, but they show the relative values of hardwoods and softwoods for acetic acid production.

Moisture Content of Wood

Moisture occurs in wood in at least two different forms: (1) the water occurring as such between the fibres of the wood and (2) the water adsorbed in the ligno-cellulose. The water occurring between the wood fibres acts like any other free water and evaporates into unsaturated air until it is all removed. The adsorbed water, however, is decreased in vapor pressure and there is a definite equilibrium between the amount of adsorbed water, the temperature, and the humidity of the air with which it is in contact. This equilibrium relation between moisture in wood and the humidity of the air is shown for three different temperatures in Figure 10.[16] This figure shows, for example, that wood in contact with air of 50 per cent humidity at 70° F. can not be dried below about 9 per cent moisture content. It shows also why "air dried" wood may vary from 5 to 25 per cent moisture depending on the temperature and humidity of the air.

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[14] Computed from results of Hunt, *West Coast Lumberman*, 1915, assuming the wood used to contain 15 per cent moisture.
[15] *Berichte 18*, 60 (1885).

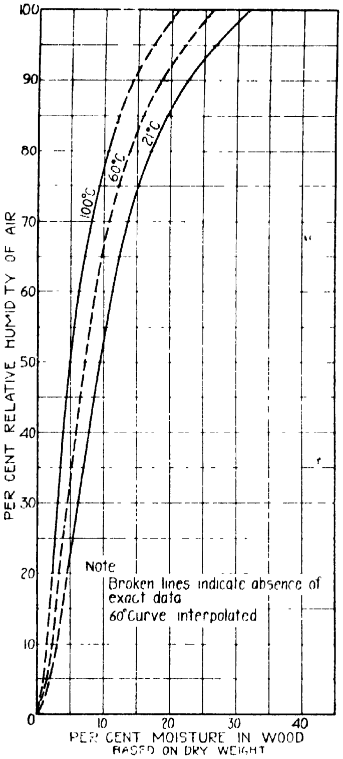

FIG. 10.—Relation between Humidity of Air and Moisture Content of Wood.

A green freshly cut piece of wood may contain as much as 100 per cent water, although the usual figure is nearer 60 per cent. Contrary to the general belief there is very little difference between the moisture content of wood from a tree cut in the summer and one cut in the winter. The question of whether the "sap is up" or "down" is not important, because the activity of the flowing sap in the spring does not necessarily mean that there is actually more sap or water in the wood at that time. The sap activity is also confined entirely to the sapwood and the heartwood is not affected.

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[16] Taken from Kiln-Drying Handbook, Dept. Agr. Bull. No. 1136. For many years the moisture content of wood has been determined on the basis of the dry weight of the wood in all the experimental work of the Forest Service. That basis is used here.

On gradually drying there is no great change in the properties of the wood until the water content is reduced to what is called the "fiber saturation point,"[17] that is, until all the free water is removed and the absorbed water begins to evaporate. As the absorbed water is removed the wood shrinks and changes in physical properties, such as strength. The effect of moisture content on the value of wood for distillation will be discussed in another chapter.

Physical Properties of Wood

It is not necessary to go into detail regarding the microstructure of wood, but a few facts on structure and physical properties will be stated which apply to the wood distillation process. The structure of wood is such that its properties are very different in different directions. It is common knowledge that wood splits with the grain more readily than across the grain, but it may not be common knowledge that wood transmits heat much more rapidly in the direction of the grain than at right angles to the grain. Liquids or vapor penetrate the wood more rapidly in the direction of the grain also and this results in a more rapid drying in this direction.

The specific gravity of wood from different species is practically the same if only the ultimate fiber is considered; the difference in gravity of large pieces of wood of different species is due to the arrangement of the fibers.[18] In the same way the conductivity of the fibers is practically the same for different species, the apparent variation being due to the structure. Dunlap[19] has determined the mean specific heat of the ultimate fiber between 0° and 106° C to be about .327 as an average of several species. He has also shown the specific gravity of several species to vary from 1.50 to 1.57.[20] These values for specific gravity were determined by floating in a concentrated solution of calcium nitrate and therefore do not represent the true specific gravity of dry wood fiber but instead that of wood fiber containing the water it holds when in equilibrium with calcium nitrate solution. This is further indicated by the fact that at 35° the gravity was found to be higher than at 30° due probably to the smaller amount of water adsorbed by the wood at the higher temperature.

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[17] Forest Service Bull. No. 40, p. 82.

[18] In some special cases the high gravity of a wood may also be due to a large proportion of extractives in its composition. This is the case with "fat" wood from longleaf pine, which contains a high proportion of resin, and quebracho wood, which contains a high proportion of tannin.

[19] Forest Service Bulletin 110.

[20] *Jour. Agr. Research,* Sept. 21, 1914.

TABLE 11.

AVERAGE WEIGHTS OF VARIOUS SPECIES OF WOOD.

Species and Locality		Weights		
		Kiln dry*	Air-dry †	Green ‡
HARDWOODS		Pounds per cubic foot		
Ash, black	Ontonagon Co, Mich.	34	36	53
" "	Marathon Co., Wis...	34	35	52
" blue	Bourbon Co., Ky .	39	41	46
" green	Richland Parish, La.	38	39	47
" green	New Madrid Co, La	40	42	49
Beech	Hendricks Co, Ind	43	45	56
"	Potter Co., Pa. .. .	4-	43	54
Birch, yellow	" " "	43	45	56
" "	Marathon Co, Wis.	43	44	59
Chestnut	Baltimore Co., Md.. .	29	30	53
"	Sevier Co, Tenn ..	29	30	56
Elm, slippery	Hendricks Co. Ind ..	42	43	53
" "	Sauk Co, Wis...	36	37	56
Gum, black	Sevier Co, Tenn	35	36	45
" red	New Madrid Co, Mo	..	35	46
" "	Pemiscot Co., Mo...	34	36	54
Hickory, big shellbark	Sardis, Miss	47	49	62
" " "	Napoleon, Ohio	55	57	65
" pignut	Sardis, Miss.	48	50	62
" "	Napoleon, Ohio	51	53	64
" shagbark	Sardis, Miss	47	49	63
" "	Napoleon, Ohio	51	54	64
Maple, sugar	Hendricks Co, Ind .	41	43	54
" "	Potter Co, Pa .	42	44	58
" "	Marathon Co, Wis .	42	44	56
Oak, California black	Butte Co, Calif..	37	38	64
" " "	Douglas Co., Oregon	39	40	68
Oak, tanbark	Willits, Calif. .. .	43	44	66
" white	Stone Co, Ark	46	48	59
" "	Hendricks Co, Ind .	46	47	61
" "	Richland Parish, La	46	48	67
Tupelo	St John the Baptist Parish, La.	35	37	66
Pine, longleaf	Nassau Co, Fla......	42	44	51
" "	Bogalusa, La.	41	42	56
" "	Lake Charles, La	42	43	45
" "	Tangipahoa Parish, La.	39	41	54
" "	Hattiesburg, Miss... .	38	40	42

* About 8 per cent moisture.
† Twelve to 15 per cent moisture.
‡ Average green material.

Table 11 gives the weight per cubic foot of various species of wood as determined at the Forest Products Laboratory in connection with their strength tests.[21] Since the specific gravity varies widely with the moisture content, the latter must always be stated in connection with weight figures.

The weight per cubic foot is an important property in connection with wood for distillation, since it governs the actual amount of wood, the weight, in the common unit of measure, the cord. Wood is commonly cut, split, hauled and sold by the cord and the capacity of the commercial distilling apparatus is determined largely by its volume. Largely on account of common practice, therefore, a light wood, such as red gum, is not so valuable for distillation as a heavy wood, such as oak, although the former may give higher yields of valuable products on a percentage weight basis. There is, however, one advantage held by the lighter wood (when compared on the cord basis), due to its lower fuel requirement of distilling and for refining the products, but this is a factor not often recognized as important and not easily determined with accuracy.

Decayed Wood

Only a little work has been done on the effect of decay on the chemical properties of wood. Rose and Lisse[22] showed that Douglas fir, a softwood, when subjected to decay loses cellulose more rapidly than any other constituent. This was confirmed by Mahood and Cable[23] and by Bray and Staidl[24] in work on the decay of a pulpwood, white spruce, also a softwood. Other changes in composition were observed but the main one of importance to wood distillation was that the cellulose was apparently attacked first and the lignin was not much affected. That is, in partly decayed wood the lignin and the methoxyl groups are in higher proportion by weight than in sound wood and, therefore, on a percentage weight basis the yields of both alcohol and acid from destructive distillation of decayed wood might be greater than from sound wood. On the other hand, from sticks of the same original weight one sound and the other partly decayed, the former would certainly give more acid and probably more alcohol. This conclusion would be a safe one only on assumption that hardwoods are affected by decay much the same as softwoods and that different kinds of decay effected by different species of fungus had much the same effect. The latter assumption is unsafe since Johnsen and Lee[25] have reported one case where decayed wood had lost lignin instead of cellulose.

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[21] Forest Products Laboratory Technical Note No. B 15

[22] *Jour. Ind. Eng. Chem.* 9, 284 (1917)

[23] *Paper* 24 (1920).

[24] *Jour. Ind. Eng. Chem.* 14, 35 (1922).

[25] *Chem. & Met. Eng.* 28, 257 (1922).

Chapter III.

The Decomposition of Wood by Heat.

The publication on wood distillation in which detailed temperature figures were first given was that of Violette.[1] He published a table showing the percentage weight of the residue from charges of wood after having been heated to different temperatures from 160° C. to the melting point of platinum. The weight at 150° C. was taken arbitrarily as 100 per cent, since it was difficult to decide where the drying of the wood ceased and the destructive distillation began. This table showed a continuous loss in weight with increasing temperature, the rate of loss being practically the same from 160° to 270° but very much slower from 270° onward. Violette's results have been used repeatedly in the literature of wood distillation even after there was plenty of evidence to question their accuracy and until very recently their accuracy has not been questioned nor has an attempt been made to study them and show why they were wrong. This was probably due to the fact that the bare table of results was copied from one publication into another until the original was forgotten and no one knew how the results were obtained. In fact, the experimental data of Violette are probably reasonably accurate and the mistake is due to applying results obtained under one special set of conditions to all other conditions of distillation. This will be discussed more in detail after the necessary information has been brought out, but meanwhile the necessity should be noted for describing in detail where the temperature is measured and how the heat is applied when reporting the results of temperature measurements on wood distillations. This is because wood is a poor conductor of heat, so that it is very difficult to heat different parts of a large charge to the same temperature at the same time and because the ordinary destructive distillation of wood is an exothermic reaction, so that the temperature in the charge may frequently be higher than that applied to the charge.

The next measurement of wood distillation temperatures was made by Chorley and Ramsay.[2] They measured the temperature at the center as well as at the surface of the charge and found that in the vicinity of 280° C. the reaction became exothermic. The more complete and detailed work of Klason, von Heidenstam, and Norlin[3] confirmed the exothermic character of the reaction, determined the amount of heat given off during the exothermic stage and, by collecting and analyzing the products at different stages, gave a complete picture of the course of the reaction. A typical diagram of the relation between the temperatures inside and outside the charge and the amount of products is shown in Fig. 11, taken from Klason's article. It is seen that no considerable amount of gas is given off until the outside temperature has reached nearly 300° C. and the inside temperature has begun to rise rapidly. Some liquid distillate is given off during the second and third half-hour periods, but this is the moisture in the wood, as shown by the inside temperature remaining near 100° C. and by the fact that the amount of distillate decreases in the next period. When the wood is dried out and the inside temperature begins to rise rapidly above 100° C. the outside portion of the charge is above 280° C. and the reaction becomes more rapid. Finally the exothermic heat carries the inside temperature above the outside and during this stage the greatest amount of gas

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[1] *Ann. Chim. phys.*, Vol 32, p 304 (1853), and Vol 39, p. 291 (1855).
[2] *Jr. Soc. Chem. Ind.*, Vol. 11, p. 395 (1892).

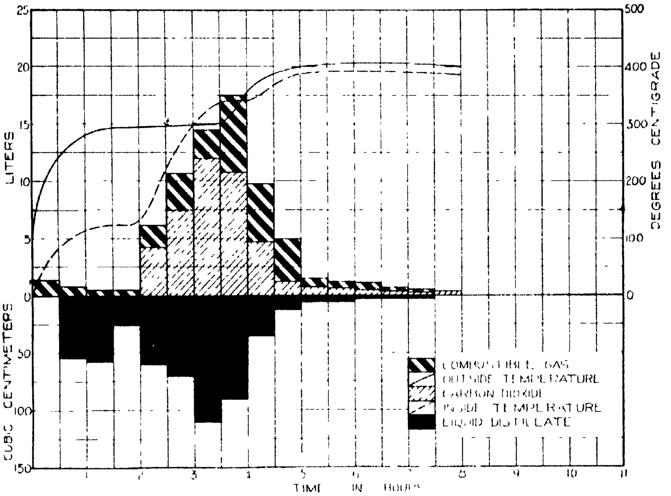

FIG. 11. - Relation between Temperature, Time and Products in Decomposition of Wood by Heat.

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[3] *Arkiv for Kemi, Mineralogi och Geologi 3*, 1-34 (1908); *Zeit. angew. Chemie*, Vol. 25, p. 1205 (1909), and Vol. 27, p. 1252 (1910).

and liquid distillate is obtained. Although the outside temperature is carried finally to 400° C., very little more distillate is obtained. The amount of combustible gas becomes greater than the carbon dioxide only after both inside and outside temperatures are above 350° C.

These results show plainly that there is very little decomposition of wood by heat at temperatures below about 250° C., but on account of other more indefinite data this conclusion must be limited to the conditions of the experiment in which the heat is applied rapidly. It is a common observation that wood subjected to long continued application of medium temperatures, as for instance in contact with steam pipes, will gradually darken and become brittle with shrinkage and loss of weight. Apparently then in long time periods wood can be decomposed by temperatures much lower than those required for distillation in a short time. Sufficient chemical change to have noticeable effect on the strength of wood may be caused by temperatures even below 100° C., but these slight changes are not of importance in connection with destructive distillation.

So far as actual destructive distillation is concerned, then, the reaction begins about 250° C., soon becomes exothermic and is finished at about 350° C. Beyond this temperature the charcoal is further decomposed, but largely into gas, no acetic acid or wood alcohol being formed. No quantitative figures are available on the amount of tar formed when charcoal is heated above 350° C., but some recent work by the author has shown that only very small amounts of tar are formed—perhaps a few tenths of a per cent.

Klason's results do not show the order in which the alcohol, acid and tar are produced, except to indicate that these products come together during the exothermic stage. It has been shown [4] that in the case of wet wood 8 to 10 per cent of the acid and 1 per cent of the alcohol may distil from the wood before actual decomposition sets in, while the water is being driven off, but this may be the result of hydrolysis and might not take place if the wood had been dried at low temperatures. Palmer [5] has also shown that the formic acid is the first important product to be formed, followed by the acetic acid, tar, and methyl alcohol in order.

Klason [6] also found that cellulose formed no methyl alcohol on distillation and this led Klar [7] to believe that, since the lignin was the source of methyl alcohol, the yield of methyl alcohol was dependent on the proportion of lignin in the wood. He then explained the higher yields of methyl alcohol from hardwoods by the higher lignin content of hardwoods. We have seen, however, that the amount of lignin in different woods does not vary enough to account for the variation in yield of methyl alcohol and that the yields of methyl alcohol do not even follow the variation in methoxyl content. (See p. 39.) Klason's second work[8] on the decomposition of wood by heat developed many more details, especially on the cause of the exothermic reaction and on the primary and secondary products. This was accomplished by distilling wood under the lowest possible vacuum and in a short time, so as to prevent the secondary reactions, and then distilling at increasing pressures and increasing lengths of time in order to obtain the secondary reactions in increasing proportions. In cathode-light vacuum and in two or three hours' time the products of distillation were very different from the usual products, especially in the composition and amount of tar and charcoal, and the progress of the reaction was different in that no exothermic heat was developed. In ordinary wood distillation processes the tar may amount to about 10 per cent of the weight of the wood and the charcoal to about 30 per cent, depending on the maximum temperature used. In this vacuum distillation the tar amounted to 43.6 per cent and the charcoal 10.4 per cent, while in a long continued (14 days) distillation under atmospheric pressure, whereby the maximum secondary reactions were obtained, the tar was 1.8 per cent and the charcoal 39.4 per cent. The 40 per cent tar obtained by vacuum distillation is different from ordinary tar in its light color, transparency and hard consistency[9]; it also decomposes exothermically at about 275° C. into water, carbon dioxide, tar coke, and ordinary tar. The exothermic character of the ordinary wood distillation reaction is, therefore, not due to the primary reaction but to a secondary reaction—the decomposition of primary tar into secondary tar, tar coke, etc. The higher yield of charcoal under atmospheric pressure is explained by the deposition of the tar coke on or in the primary charcoal and ordinary charcoal must, therefore, be considered as primary charcoal plus tar coke.

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[4] Hawley and Palmer, Dept. Agr. Bull. No 129.
[5] *Jour. Ind. & Eng. Chem.*, Vol. 10, p 260 (1918).
[6] *Loc. cit.*
[7] Technologie der Holzverkohlung, Second Edition, p. 12.

This conception of ordinary charcoal as primary charcoal in which secondary tar coke has been deposited is somewhat at variance with Chaney's theory[10] of charcoal as "a stabilized complex of hydrocarbons adsorbed in a base of active (absorptive) carbon." Chaney has shown the presence of hydrocarbons with boiling points around 300° C. in charcoal which had been previously heated to 850° C. and assumes that the process of activating charcoal consists in the removal of these adsorbed hydrocarbons by heat or selective oxidation. In Klason's conception of the composition and formation of charcoal some adsorbed hydrocarbons may be present, but there is another component which must also be removed to render the charcoal absorbent, viz., the tar coke which has been deposited on the primary charcoal. If we consider that the primary charcoal of Klason is absorptive the activation of ordinary (secondary) charcoal would consist in removing the tar coke and the adsorbed hydrocarbons. It would be easy to prove or disprove this theory by preparing primary charcoal by distillation of wood in vacuum and testing its absorptive qualities. It has been claimed that the charcoal obtained by distilling wood in a current of hot gases is much more absorptive than ordinary charcoal and if true this would confirm the theory, since the same conditions of rapid removal of primary products exist in a current of hot gas as in a vacuum and there would be a tendency to form primary charcoal

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[8] *Jour. für prakt. Chem.* (2), 90, 413 (1914).

[9] The composition of this tar was not studied, but in view of the results of Pictet and Sarasin, *Compt. rend.*, 166, 38 (1918), on the distillation of cellulose in a vacuum it would be very interesting to see whether it contained levoglucosan.

[10] *Proceedings, Am. El. Chem. Soc.*, 1919.

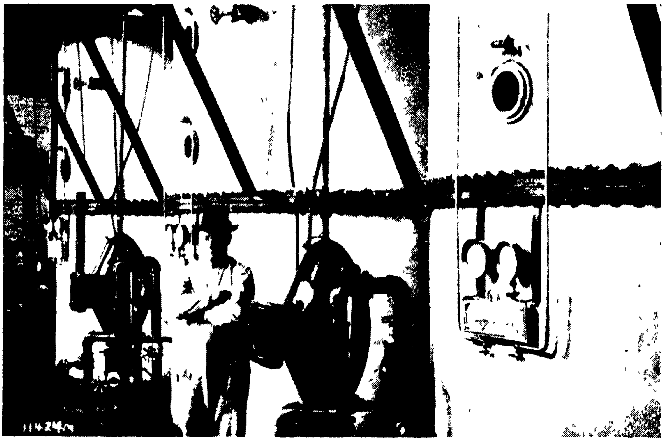

FIG. 12 Triple Effect Pyroligneous Acid Evaporators.

With detailed information available on the mechanism of wood distillation it is now possible to offer some explanations for the fact that Violette's figures do not correspond with those of Klason on the relation between temperature and percentage of charcoal. Violette's distillations were carried out by means of superheated steam in contact with the wood as a heating medium and the recorded temperatures were measured in the outlet from the distilling vessel. These conditions offer several reasons for variation from Klason's results. The presence of a rapid current of superheated steam in contact with the small pieces of wood (cylinders ½″ x 1½″ were used) may have made the conditions sufficiently like those of vacuum distillation, so that the exothermic reaction was not noticeable; there may have been a reaction between the wood and the heating medium, (steam) which complicated the results of the main reaction of the decomposition by heat; the temperature measured only at the outlet of the retort only did not represent the actual temperatures to which the wood was subjected. With all these possible reasons for error there seems to be no further reason for applying Violette's figures to the ordinary distillation of wood.

Methyl alcohol and acetic acid were found by Klason to remain practically constant over the entire range of conditions from distillation in cathode light vacuum to 14-day distillation at ordinary pressure. A slight decrease in acetic acid with increasing time was balanced by an increase in acetone, showing that the latter is a secondary product obtained at the expense of the former. Alcohol and acid are then primary products and within limits are not affected by the conditions of the distillation. This at first seems at variance with Palmer's results[11] in increasing the yields of alcohol and acid in commercial operations by controlling the conditions of firing and also at variance with the common experience of plant operators that a carefully fired 36-hour distillation will give higher yields than a more rapid 24-hour cycle. These two sets of results can be reconciled, however, when we consider the different conditions under which they are obtained, in one case with very small evenly heated apparatus, in the other with large apparatus heated mostly on the bottom.

In the first case the secondary reactions are affected more by the time the primary products remain in the heated zone than by the temperature of superheating, because the various speeds of distillation can be obtained with only slight differences in the maximum temperature. In this case, therefore, rapid distillation results in minimum secondary reactions (especially when aided by high vacuum). In the other case of large scale commercial apparatus the usual speeds of distillation are very rapid, considering the size of the distilling vessel and the length of time required for the heat to penetrate to the center of the charge of wood, and the speed can be varied only by wide variations in the maximum temperatures to which the retort is heated. The secondary reactions are, therefore, affected more by the variations in temperature than by the corresponding variations in the time during which the products are subjected to the high temperatures. In very small apparatus, therefore, methyl alcohol and acetic acid may be primary products not greatly affected by variations in the speed of distillation, but in large commercial apparatus the superheating is so great that new secondary reactions may take place, such as the decomposition of methyl alcohol and acetic acid, and these secondary reactions will be increased by greater speed of the distillation, since increased speed can be obtained only by higher temperatures.

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[11] *Jour. Ind. Eng. Chem.* 7, 663 (1915).

Formic acid is more influenced by the conditions of distillation than any other of the single simple products, while acetic acid is practically constant. The ratio between the two, the "formic acid number" of Klason, can, therefore, be used to determine the amount of the various secondary reactions. In vacuum distillation the formic acid number (the parts of formic acid to 100 parts acetic acid) is 34 and this gradually decreases till with 14-day distillation at atmospheric pressure it becomes 5. In commercial operations, especially in continuous processes where the true temperature and speed are difficult to determine, this formic acid number might be valuable to determine the amount of superheating.

Klason in this study has also made the first quantitative determinations of formaldehyde in wood distillation products. He found from 1.27 per cent in vacuum distillation to 0.80 per cent in 14-day distillation. He states that formaldehyde is not noticed in commercial products, since in one of the early steps of refining, the neutralization with lime, it undergoes self-contained oxidation and reduction to methyl alcohol and formic acid.

It is now possible to speculate on the possible effect of varying moisture content of the wood on the yields. Klar[12] says that plant experience shows that the yields of acid are inversely proportional to the water content of the wood. In another place,[13] however, he says that absolutely water-free wood does not give so good yields as wood with 10 to 20 per cent moisture. Palmer[14] has made a study of this question in small scale apparatus and found that the effect varied with the species and with the speed of the distillation so that no general conclusions can be drawn. His work was done, however, in apparatus in which the temperature conditions could not be varied widely (an oil bath was used for heating) and the variations in moisture content were also not very great. In commercial apparatus, therefore, there may be a general relation between moisture content and yields of acid and alcohol, but this has not yet been definitely developed. It is possible that the main effect of water is to regulate the speed of this distillation, as pointed out by Klar[15] and this effect would, in general, be favorable. It is certain that low moisture content is favorable from the standpoint of low fuel requirements for distilling the wood and refining the products, but the balance between this effect and that on yields has not been determined.

The details of the progress of the distillation throughout the charge

[12] *Loc. cit.*, p. 77.
[13] *Loc. cit.*, p. 21.
[14] *Jour. Ind. Eng. Chem.* 10, 262 (1918).
[15] *Loc. cit.*, p. 39.

of wood in commercial apparatus have not been worked out and there are various views as to the exact means by which the wood is heated-- by convection, radiation or conduction. When we consider the low heat conductivity of wood it is difficult to comprehend how such a large mass can be completely distilled in such a short time. The wood is in large sizes, with the greatest dimension in the direction of the greatest conductivity (with the grain), and does not come directly in contact with the heated walls of the retort, so that except for the small amount of heat transmitted to the wood through the cars it must be heated by radiation or convection. On account of the low conductivity of wood it seems impossible that the wood in the center of the charge can be heated by conduction through the wood from the surface of the charge, and if piled at all closely direct radiation of heat from the walls of the retort could not reach all parts of the charge, so that convection currents must be responsible for a part of the heating. When we remember also that the wood often contains 25 to 35 per cent water which must be removed before destructive distillation will take place, the problem becomes even harder. Without the aid of the exothermic reaction it is doubtful if wood could be distilled in any practical length of time in the modern large oven. This "interior heating" amounts to about 2.5 per cent[16] of the fuel value of the wood and would, therefore, be equivalent to the vaporization of 20 per cent water from the wood. The exothermic reaction must, therefore, play a large part in the distillation of such a non-conductor as wood.

Decomposition in the Presence of Chemicals

The first work on this subject was by Palmer,[17] who distilled maple and beech chips which had been treated by boiling and cooling in a solution of phosphoric acid. With 7.6 per cent phosphoric acid, maple showed a considerable increase in alcohol but none in acetic acid. Beech treated with phosphoric acid in quantities from 4.8 per cent to 9.7 per cent gave large increases in both alcohol and acetic acid. There distillations have been repeated[18] on maple wood, using a different method of distillation without obtaining the large increase of alcohol reported by Palmer, but in one respect the results were the same. With as small an amount of phosphoric present as 3 per cent the settled tar was negligible and the soluble tar was greatly reduced. This is the most striking result of treating the wood with phosphoric acid.

Palmer also made a few distillations with phosphoric acid in which the pressure in the autoclave was allowed to rise to 60 and 100 lbs.

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[16] Klason, *loc. cit.*
[17] *Jour. Ind. Eng. Chem.* *10*, 264 (1918).
[18] Hawley, *Jour. Ind. Eng. Chem.* *14*, 43 (1922).

per sq. in., but the yields of both alcohol and acid were reduced by these conditions except in the case of one erratic and unchecked run in which a very high acid yield was recorded.

Although probably not an effect due to the action of chemicals on the yield from the wood, another experiment reported in the same paper by Palmer will be noted. By mixing equal parts of wood and crude wood creosote and distilling under pressures he obtained very high yields of alcohol. With pressures of 30, 60 and 90 lbs. the increase in alcohol due to the presence of the creosote was 1.46 per cent, 1.75 per cent and 2.10 per cent, respectively (based on the weight of the wood). At ordinary pressures no increase of alcohol was obtained from the mixture with creosote. Since these increased yields of alcohol may be due to the decomposition of the tar when distilled under pressure, the results will not be discussed further.

In 1854 Fremy [19] reported that various cellulosic materials, including wood, gave large yields of acetone when distilled in the presence of 8-10 parts of lime, the acetone being much more than the equivalent of the acetic acid obtained by the destructive distillation of the same materials without lime. Basset [20] confirmed these results in the case of wood and stated that as little as two and one-half parts lime to one of wood gave a yield of 26 per cent acetone and mixed ketones. In neither of these cases was the alcohol yield reported. In distilling wood with very much smaller quantities of lime it was found [21] that no increase in acetone was obtained, although the acetic acid was very much diminished, but that the methyl alcohol was increased. In trying other "catalyzers" in order to find one which would perhaps increase the alcohol without diminishing the acid, it was found that calcium carbonate in large proportion (50 per cent the weight of the wood) and sodium carbonate in as small an amount as ½ per cent would accomplish this. With maple wood an increase of 40 per cent in the alcohol yield can be obtained by treating the wood with 1 per cent sodium carbonate previous to distillation and with oak wood the alcohol yield was doubled under similar conditions. The acid yield is decreased very slightly, if at all, and the acetone is not increased. Other mild alkalies such as sodium silicate give similar results. A large number of other catalyzers have been tried without any promising results.

In order to get these favorable results it is necessary to have the wood evenly treated with the sodium carbonate. In the case of treated blocks 6 inches long in which the ends and the sapwood only were penetrated by the solution, the effect of the sodium carbonate was dimin-

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[19] *Ann Chem. 15*, 279.

[20] *Chem. & Met Eng 20*, 190 (1919).

[21] Hawley, *Jour. Ind. Eng. Chem. 14*, 43 (1922).

TABLE 12.

YIELDS FROM THE DISTILLATION OF WOOD IN THE PRESENCE OF CHEMICALS.

Wood		Catalyzer		Method of treatment	Alcohol	Acetic acid
Species	Size	Kind	Amount			
Maple	Sawdust	....	....	....	1.61	5.22
"	"	H_3PO_4	0.5	Soaking	1.51	5.67
"	"	"	1.0	"	1.25	5.39
"	"	"	1.5	"	1.55	5.40
"		$Ca(OH)_2$	Equiv to 60 per cent CaO	Mixing	2.45	0.48
"	"	$CaCO_3$	Equiv to 40 per cent CaO	"	2.08	4.64
"	"	"	Equiv to 10 per cent CaO	"	1.80	5.20
"	"	Na_2CO_3	1.5	Soaking	2.39	5.26
"	"	"	1.0	"	1.94	5.02
"	"	"	0.5	"	1.61	5.32
"	"	Na_2SiO_3	3.0	"	2.21	5.77
White oak	"	....	..	....	1.17	4.91
" "		Na_2CO_3	0.5	"	2.58	5.09
" "	"	"	1.0	"	1.99	3.86
" "	"	"	1.5	"	2.47	3.40
Maple	6" blocks	....	..	....	1.67	6.75
"	"	Na_2CO_3	0.68	Pressure	2.09	5.52
"	"	"	1.12	"	2.16	6.74
"	"	"	3.15	Soaking	1.80	4.35
White oak	"	..	..	......	1.20	5.56
" "	"	Na_2CO_3	0.52	Pressure	1.85	4.71
" "	"	"	1.03	"	1.79	5.58
" "	"	"	1.26	Soaking	1.40	5.66

per sq. in., but the yields of both alcohol and acid were reduced by these conditions except in the case of one erratic and unchecked run in which a very high acid yield was recorded.

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In order to get these favorable results it is necessary to have the wood evenly treated with the sodium carbonate. In the case of treated blocks 6 inches long in which the ends and the sapwood only were penetrated by the solution, the effect of the sodium carbonate was diminished. Table 12 shows some of the results obtained with various catalyzers and methods of treatment.

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[19] *Ann Chem.* *15*, 279.
[20] *Chem. & Met Eng* *20*, 190 (1919).
[21] Hawley, *Jour. Ind. Eng. Chem.* *14*, 43 (1922).

In order to get these favorable results the distillations must be carefully controlled. The exothermic reaction is apparently intensified and if the charge is heated too rapidly the distillation becomes uncontrollable, with the result that the yields of both acid and alcohol are reduced. The full yields of acid obtained under the proper conditions are difficult to explain on account of the presence of an alkali. The alkali has been leached from the charcoal in several cases and found to be converted to acetate only to the extent of 16 per cent at the maximum.

The reason for the increase in alcohol yield when wood treated with sodium carbonate is distilled has not been determined, but the source of the increase in alcohol has been found. It was stated in the chapter on the chemical composition of wood that hardwoods contained about 4 times as much methoxyl as was converted into alcohol by distillation of the wood Table 13[22] shows the distribution of the methoxyl groups in the products of the distillation of maple and oak wood. Only about 70 per cent of the methoxyl in the original wood is recovered in recognizable form in the products (including methane in the gas), the remainder being converted into some other products not recognizable as methoxyl derivatives. The table also shows the effect on the distribution of methoxyl derivatives when sodium carbonate treated wood is distilled. In the case of maple wood it is seen that the increase in methoxyl in the pyroligneous acid (increase in methyl alcohol) is just about balanced by the sum of the decreases in the charcoal and the dissolved tar and, therefore, the source of the increased methyl alcohol is the methoxyl groups usually occurring in the settled tar and the charcoal.

In the case of oak wood the distribution of the methoxyl groups in the distillation products is much the same, except that the amount in the pyroligneous acid is less and the amount in the charcoal is considerably greater than with maple wood. On distilling oak in the presence of sodium carbonate the decrease in methoxyl content of the charcoal and the dissolved tar is not quite enough to account for the increase in the methyl alcohol, but there is a very marked decrease in the methane content of the gas, which may account for the rest. The total recovered methoxyl is also diminished by the sodium carbonate.

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[22] Hawley and Aiyar, *Jour. Ind Eng Chem* 14, 1055 (1922).

Chapter IV.

Products of Wood Distillation.

The products of wood distillation will be discussed according to the groups in which they naturally separate on distilling the wood and condensing and settling the condensible products, i.e., gas, pyroligneous acid, settled tar, and charcoal. It must be understood at the beginning that the yield and composition of these groups will vary with the kind of wood distilled and with the conditions of the distillation, so that only general figures can be given. It must also be understood that there is much overlapping of these groups, small amounts of the typical constituents of one group being found in one or more of the others.

Gas

The composition of the gas has been reported on by several observers, so that its main constituents are well known. Klar [1] states that the average composition of the gas from a commercial plant is as follows:

Carbon dioxide	59 per cent by vol.
Carbon monoxide	33
Methane	3.5
Hydrogen	3.0
Vapors	1.5

He also gives the yield of gas as about 240 cu. ft. per hundred pounds of wood or roughly 8,000 cu. ft. per cord. The fuel value of the gas from 100 Kg. of wood is computed by Klar to be equivalent to 2.59 Kg. of coal with 5,000 "available" calories per gr., or the gas from one cord (3,300 pounds of dry wood) would be equivalent to 85 lbs. of coal of 9,000 "available" B.t.u. per pound. Klason [2] shows the gas from small scale experiments to contain more methane and less hydrogen than is given by Klar and the figures in Table 13 also show more methane, but Klar's figures may be correct for commercial samples of wood gas.

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[1] *Loc. cit.*, p. 44.

[2] *Loc. cit.*

Bergström and Wesslén[3] give the following data on the gas obtained from air dry softwoods in Swedish ovens heated by flues within the oven:

Carbon dioxide	50 per cent
Heavy hydrocarbons	3
Carbon monoxide	28
Methane	18
Hydrogen	1

They also give the yield of this gas as 18 per cent by weight on the dry wood distilled or about 4,600 cu. ft. per cord. It seems likely that the figure for methane in this table is too high, since it would require nearly all the methoxyl in the original wood in order to give this percentage of methane in the gas, and it has already been shown that other products of distillation beside the gas contain high proportions of methoxyl.

The 1.5 per cent "vapors" shown as part of the gas constituents are made up of all the volatile constituents of the two other groups, pyroligneous acid and tar, the most volatile constituents naturally being present in the higher proportion. This point will be discussed further under refining methods.

Pyroligneous Acid

The pyroligneous acid is a very complex mixture, only a few of whose constituents have been identified. It contains from 80 to 90 per cent of water, of which part is the moisture in the wood distilled and part (about 20 per cent of the weight of the dry wood) is formed by the decomposition of the wood. Following is a list[4] of the products which have been reported, not including those found mainly in the tar and occurring only in small quantities in the pyroligneous acid:

Formic acid
Acetic acid
Propionic acid
Butyric acid
Valeric acid
Caproic acid
Crotonic acid
Angelic acid
Methylamine
Isoamyl alcohol
a-Methyl β keto-pentamethylene
Pyromucic acid
Methyl alcohol
Allyl alcohol
Acetaldehyde
Furfural
Methylfurfural
Acetone
Pyroxanthen
Methyl formate
Methyl propyl ketone
Pyridine
Methyl ethyl ketone
Ethyl propyl ketone
Dimethyl acetal
Methylal
Valero lactone
Methyl acetate
Pyrocatechin
Ammonia
Isobutyl alcohol
Keto-pentamethylene
Methyl pyridine

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[3] Om Trakolning, p. 213

[4] Muspratt, Vol. II, p. 1869, as given by Klar, *loc. cit.*, p. 51, and Fraps, *Am. Chem. Jour.* 25, 26 53.

To these should be added formaldehyde as shown by Klason (see page 56).

Acetic and formic acids, methyl and allyl alcohols, acetone and methyl acetate are the most important and occur in greatest quantities, being the only ones separated or recognized in the refining process except for the "alkaline constituents" separated by acid treatment in refining the alcohol. Except for some of these important constituents there are no quantitative data on the composition of pyroligneous acid.

Pyroligneous acid also contains from 7 to 12 per cent of soluble tar but this will be discussed under the composition of the settled tar, since it is probably made up mostly of constituents the same as those occurring in settled tar. Certain heavy oils are also contained in solution in the pyroligneous acid[5] but they too are made up of constituents occurring mostly in the tar. Pyrocatechin in the list above is one of these and should not be mentioned in preference to many other phenolic bodies which also occur in both the tar and the pyroligneous acid. After the pyroligneous acid has been distilled from the non-volatile settled tar and neutralized with lime other non-volatile compounds are produced as shown by the insoluble "sludge" and by the soluble material which remains as an impurity in the acetate of lime. The composition of these non-volatile products in the neutralized pyroligneous acid is unknown and the compounds from which they may have been formed can only be guessed at. Di-acetyl has been identified in the products of resinous wood distillation[6] but very likely it is a product of the lignocellulose and occurs also in hardwood distillates. This is a compound which would distil with the pyroligneous acid and on neutralization would polymerize to an insoluble product, xylochinon, which would contaminate the acetate. The organic impurities in the acetate are probably formed from similar complex di-ketones or aldehydes which polymerize on neutralization.

Tar

The tar is a very complex product of which only a few constituents have been identified. It consists of all the substances previously mentioned as constituents of the pyroligneous acid together with "light oils," "heavy oils" and pitch. The light oils (with boiling points below 140° C.) have been studied by Fraps[7] and a series of acids and ketones have been identified. A complete list of identified substances is given below:

[5] Hawley, *Chem. & Met Eng.* 25, 197 (1921).

[6] Aschan, *Zeit. fur angew Chem.* 1907, p. 1811.

[7] *Am. Chem. Jour.* 25, 26-53.

Valeric aldehyde
Acetone
Methyl ethyl ketone
Methyl propyl ketone
Methyl butyl ketone
Adipic ketone
Nitriles
Di-methyl furane
Unsaturated compounds
m-xylene
Polymerized compounds
Methyl acetate
Methyl propionate
Methyl n butyrate
Methyl n-valerate
Esters of unsaturated acids
Sylvane
Di ethyl ketone
Tri methyl furane
Toluene
Hydrochloric acid addition products

Few quantitative data are given and no indication of what proportion of the oils is made up of unidentified constituents. Probably there is a large proportion of less reactive constituents, such as hydrocarbons, which have not been identified

The heavy oils (heavier than water with boiling points above 200° C.) have been rather thoroughly studied so far as the alkali soluble constituents are concerned. The following list is taken from Beilstein, all the phenols being included which are there mentioned as having been found in wood tar:

Phenol
o-, m- and p-cresol
Phlorol
1-3 xylenol-5
1-3 xylenol-4
Pyrocatechin
Guaiacol
Di methyl ether of homopyrocatechin
Coerulignol
Pyrogallol
Pyrogallol di-methyl ether
Methyl pyrogallol di-methyl ether
Propyl pyrogallol di methyl ether
Creosol

Besides most of this list ethyl guaiacol is mentioned by Fraps.[8]

No quantitative data on single compounds are available, but from the boiling points and gravities a rough grouping of the constituents can be made. (1) Phenol and the cresols occur only in very small quantities because the alkali soluble constituents of wood tar begin to boil very close to 200° C., thus excluding phenol and ortho cresol while the gravity of the fractions in the vicinity of 200° is higher than the other cresols, showing that they can occur only in small proportion. (2) The largest portion of the alkali soluble constituents boil between 200° and 235° C. and, therefore, includes phlorol, the xylenols, guaiacol, cresol, and homopyrocatechin di-methyl ether. (3) The rest of the phenols mentioned boil above 240° C. and constitute the second largest group in total amount. The alkali insoluble constituents of the heavy oils have not been studied, but probably contain the higher members of the series found in the light oils such as ketones and "unsaturated compounds," together with the higher phenol methyl ethers.

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[8] *Loc. cit.*

The composition of the pitch is unknown. A part of it is probably formed by the polymerization of complex aldehydes and ketones, and it has been suggested that part of it is of the nature of the aldehyde-phenol resins, since both aldehydes and phenols are among the products of wood distillation. Klason has shown, however, that there is little pitch in the primary products of distillation and that most of it must be a product of the decomposition of the primary tar. We would, therefore, expect it to consist largely of the higher members of the groups found in the oils, namely, ketones, methoxyl ethers of the phenols and possibly hydrocarbons.

A typical hardwood tar contains about 11 per cent water (and water soluble constituents separating with the water on distillation) and 12 per cent light oils with gravities below 1.0. The change from "light oils" to "heavy oils" takes place as the temperature of distillation reaches about 180° C. (measured in the vapors). The proportions of heavy oils and pitch vary with the conditions of distillation and the consistency of the pitch. If, for instance, the oils are distilled only to a temperature of 240° C., 25 per cent heavy oils will be obtained and the pitch residue will be very soft. If the distillation is carried to 270° C. (about the highest that can be obtained without decomposition) the heavy oils will amount to 42 per cent and the pitch will be harder. If a current of air is run through the still to help carry over the vapors, 52 per cent heavy oils are obtained and the residue is a hard brittle pitch. By coking the pitch a maximum of about 58 per cent heavy oil can be obtained.

TABLE 14.

FRACTIONS OF WOOD TAR OIL.

Fraction ° C.	Volume Cc.	Weight grams	Per cent by volume of entire distillate
93–115	700	700.46	6.23
115–195	840	844.20	7.40
195–210	815	811.84	7.10
210–215	445	443.22	3.89
215–220	840	867.72	7.72
220–225	590	605.34	5.40
225–230	805	821.50	7.20
230–235	1,000	1,029.60	9.06
235–240	1,000	1,020.50	9.04
240–245	480	496.80	4.36
245–250	740	771.82	6.77
250–255	515	532.51	4.67
255–265	1,375	1,442.38	12.66
265–280	950	979.93	8.60
Total	11,155	11,385.62	100.00

These figures are much the same as those given by Judd and Acree,[9] except that their tar contained an unusual amount of water and their distillations were not carried to the coking of the pitch.

Table 14[10] shows the boiling point and percentage volume of the fractions obtained on redistilling the total oils from a hardwood tar.

These figures on tar composition do not agree with those given by Klar[11] in that the percentage of oils is much higher and the percentage of pitch correspondingly lower. This can be accounted for only by difference between the commercial hardwood tars produced in Europe and this country.

Charcoal

The charcoal is so complex that no single chemical constituent has ever been separated and identified. It has been shown to contain methoxyl groups, however (see p. 60), and may be considered as consisting of still higher members of the series found in the tar and the pitch (the secondary charcoal constituents, see p. 53) deposited on the primary charcoal, which as the residue of the lignocellulose decomposition is probably more complex than the original raw material.

TABLE 15

Amount and Composition of Charcoal Produced at Different Maximum Temperatures

Distillation temperature	Composition of charcoal			Yield of charcoal in percentage weight of dry wood
	Carbon	Hydrogen	Oxygen, etc	
° C.	Per cent	Per cent	Per cent	
200	52.3	6.3	41.4	91.8
250	70.6	5.2	24.2	65.2
300	73.2	4.9	21.9	51.4
400	77.7	4.5	18.1	40.6
500	80.2	3.1	16.7	31.0
600	92.2	2.6	5.2	29.1
700	92.8	2.4	4.8	27.8
800	95.7	1.0	3.3	26.7
900	96.1	0.7	3.2	26.6
1000	96.6	0.5	2.9	26.8
1100	96.4	0.4	3.2	26.1

It has been stated previously that the amount and composition of the charcoal varies with the maximum temperature to which it has been subjected. These variations are shown quantitatively in Table 15 taken from Bergström and Wesslén.[12] This table is subject to some of the same criticisms as Violette's figures on the same subject (see p. 54). It is not stated where the temperatures were measured, and on account of the impossibility of heating all parts of the wood or charcoal to the same temperature at the same time, these temperatures can be only relative and average. The authors, however, recognized this condition and offered the figures for their relative values, stating that they were the result of small scale determinations and that they would not be applicable under all conditions.

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[9] *Jour. Ind Eng Chem.* 9, 276 (1917)

[10] Taken from Pieper, Acree and Humphrey, *Jour Ind. Eng. Chem.* 9, 463 (1917).

[11] *Loc. cit.*, p. 57.

It is seen that the yield of charcoal at 400° C., the temperature usually obtained in practice, is 40.6 per cent and that this coal contains 77.7 per cent carbon. As the maximum temperature increases, the yield of charcoal decreases, the percentage of carbon in the charcoal increases and the hydrogen and oxygen decrease. The yield of charcoal at 400° C. corresponds fairly well with the yields shown in Table 5, since it is a little lower than the average of Table 5 but was obtained at a somewhat higher temperature.

TABLE 16

AMOUNT AND COMPOSITION OF GAS FROM CHARCOAL AT VARIOUS HIGH TEMPERATURES

Temperature ° C.	Cc gas per gr dry and ash free charcoal		Composition of gas in percentage volume							
			A				B			
	A	B	CO_2	CO	CH_4	H	CO_2	CO	CH_4	H
420	7.2	3.3	63.2	22.9	6.2	7.7	28.4	32.0	33.1	6.5
420-520......	9.5	10.7	11.6	52.5	15.0	20.9	9.1	55.0	27.5	8.4
520-600......	16.4	17.9	15.5	37.7	25.5	21.3	19.0	36.6	30.0	14.4
600-700......	32.0	40.7	13.6	19.8	23.4	43.2	2.8	17.9	31.8	47.5
700-800......	55.2	58.6	2.0	10.4	22.5	65.1	0.6	13.1	30.5	55.8
800-900......	43.0	45.3	1.1	2.3	14.7	81.9	0.1	3.4	12.8	83.7
900-1000.....	41.5	23.3	1.1	1.9	2.8	94.2	0.0	2.2	6.8	91.0

A and B different samples of charcoal.

The amount and composition of the gas given off when a charcoal is heated to various temperatures higher than that at which it was produced is shown in Table 16, also taken from Bergström and Wesslén.[13]

The methane content of the gas from sample B when calculated to methoxyl gives nearly 7 per cent methoxyl on the weight of the charcoal, or about 2.5 per cent on the weight of the original wood. This is more methoxyl than has been found in charcoal by analysis (see p. 60) and indicates either that some of the methoxyl groups in charcoal are so inactive that they are not acted on by the analytical treatment or that at these higher temperatures some methane may be formed from some other source besides methoxyl groups. The former is the more likely assumption.

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[12] *Loc. cit.*, p. 174.
[13] *Loc. cit.*, p. 180.

The nitrogen content of two samples of charcoal is given by Bergström and Wesslen as 0.15 per cent. This indicates that about one-fourth of the nitrogen in the original wood remains in the charcoal.

In general then the distillation of wood produces in large amount certain very simple substances as water, carbon dioxide, methane, acetic acid, methyl alcohol, formaldehyde, and acetone, and in much smaller amounts the higher homologues of some of these simple compounds; the pyrrol ring is represented by a few compounds and the benzene ring is found almost entirely in the alkali soluble constituents of the tar. Polymerization and condensation products of the simpler compounds are found probably along with the still higher members of the series mentioned, which are so complex and inactive that they can not be identified. Most of the products are less complex than the original lignocellulose, but the charcoal and probably part of the pitch are apparently residues of even more complex composition than lignocellulose.

From these general statements the lignocellulose can be pictured as containing hydroxyl, methoxyl, acetyl and formyl groups on a structure of benzene and pyrrol rings. Whatever other structures may be present are not indicated by the distillation reaction.

The marked differences from the products of distillation of coal are in the lack of nitrogen compounds, of benzene, naphthalene, anthracene and similar hydrocarbons, and of the simple phenols; and in the presence of the compounds with methoxyl, formyl and acetyl groups.

Chapter V.

Refining Processes.

The discussion of the refining processes from the standpoint of the chemistry involved will be taken up first according to the general commercial process of complete cooling of distillate as soon as it leaves the retort, resulting in the separation of the non-condensible gas from the liquid products, followed by settling the liquid products to separate the pyroligneous acid from the tar. Then other more complicated systems will be discussed.

Gas

The condensation of vapors of volatile liquids when mixed with non-condensible gases is a more difficult problem than when the vapors occur alone. This is for the reason that the uncondensed gases tend to carry a part of the condensible products with them as they leave the condenser outlet. The condensible products carried in the vapors are in two distinct forms and require different means for their recovery. The first and most obvious form in which these products are carried in the gas is as a fog or mist, that is, in fine droplets of liquid so small that they settle out only very slowly, if at all. The exact cause of this fog formation is not known and it is a question whether different conditions of condensation may vary the amount of fog. It is certain, however, that it is not due to inefficient condensation, since the particles are in liquid form and may be carried by a perfectly cool gas. These small particles can be stopped only by some mechanical means such as baffle plates, a scrubbing tower, or an electrostatic precipitator. The slow and incomplete settling noticed in the gas mains is due to the larger particles only, and even greater retardation of the speed of the gas flow, as in a gas tank, would probably not settle the finer particles in any reasonable length of time. Baffle plates in large gas mains would probably stop some more of the fog by the contact of the particles with the wet plates, but a scrubbing tower filled with coke or provided with water sprays would be more efficient.

It is doubtful, however, whether any of these means of stopping the fog would give a complete separation. The problem is similar to that in other industries where liquid particles like SO_3 fog or solid particles like cement dust are carried in gases. In these cases complete and rapid settling can be obtained only by an electrostatic precipitator.

It has been reported[1] that a Cottrell precipitator was installed on the outlet from the condenser of a wood distillation oven with complete settling and recovery of the fog. The amount of liquid recovered was about 1.7 per cent of that coming from the condenser in liquid form, and the composition was about the same except that there was not quite so high a proportion of the more volatile products, such as alcohol.

The second form in which condensible products may be carried away from the condenser by the gas is as a true vapor. This is due to the fact that the condensed liquid has a slight vapor pressure even when well cooled and the gas is, therefore, saturated with the vapors, the proportion of vapors in the gas depending entirely on the vapor pressure and the vapor pressure varying with the temperature. If, for instance, the liquid condensate has a vapor pressure of 17.4 mm, the gas will consist of $\frac{17.4}{760}$ or 2.3 per cent of vapors by volume. This vapor pressure of 17.4 mm is actually that of water at 68° F., which is an indication of the possibilities of loss in this way. The vapor pressures also increase rapidly with increasing temperature, so that, for instance in the case of water, the vapor pressure is more than doubled between 68° F. and 90° F. In fact, the loss of vapors would naturally be greater than this since the more volatile constituents of the pyroligneous acid, methyl alcohol and methyl acetate, have much higher vapor pressures than water (88.7 mm and 169.8 mm, respectively, at 20° C.) and the vapor pressure of the pyroligneous acid would probably be higher than that of pure water. In this case also the composition of the lost vapors would be different from that of the pyroligneous since the more volatile constituents would be lost in greater proportions. It should also be noted in this connection that in this unneutralized pyroligneous acid a fairly large proportion of the methyl alcohol exists in the form of methyl acetate which is subsequently hydrolized to methyl alcohol by the neutralization. The methyl acetate having a higher vapor pressure than methyl alcohol goes into the gas in greater quantities than pure methyl alcohol would.

Klar[2] says that losses in the gas of 5 per cent of the total acetic acid and methyl alcohol have been observed by him.. Lawrence[3] says that 5 per cent of acetic acid and 45 per cent of the alcohol may be lost in the gas but such a high loss of alcohol seems improbable except in case of very poor cooling. In the case of the kiln process where the proportion of gases is higher, due to the admission of air to the kiln and the partial combustion of the charge, a loss of wood alcohol constituents amounting to 35 to 40 per cent of the total has been observed.[4]

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[1] Unpublished report of the Research Corporation

[2] *Loc. cit.*, p. 61.

[3] *Jour. Soc. Chem. Ind.* *37*, 13T (1918).

The vapors of alcohol, methyl acetate, and acetone can be partly recovered by running the gases up through a scrubbing tower in which they are washed by a descending stream or spray of water, since all of these vapors are soluble in water and their vapor pressure is diminished by solution in water. Probably a non-volatile or high-boiling oil such as is used in toluene recovery from coal gas could also be used efficiently for scrubbing a wood gas.

Liquid Products

The liquid products from the condensers on standing separate into two liquid layers, the tar and the pyroligneous acid, the tar on account of its higher specific gravity settling to the bottom. On account of mutual solubility, however, the separation is not complete, a part of the oils and of the non-volatile constituents of the tar remaining dissolved in the pyroligneous acid and part of the water, acid and alcohol, of the pyroligneous acid remaining dissolved in the tar. According to Klar[5] European hardwood tars contain about 18 per cent water, 2 per cent acetic acid and 0.7 per cent wood alcohol. The tars produced in the typical American plants will often contain 3.5 to 4.0 per cent acid, and hardwood tars produced in the laboratory have run as high as 7 per cent acid. There are probably several reasons for these variations but one of them is certainly the difference in the acid concentration of the pyroligneous acid. It would be expected that a tar in contact with a pyroligneous acid containing a high concentration of acetic acid would also contain a high concentration of acetic acid.

The amount of "soluble tar" and oils in the pyroligneous acid is also variable. Klar[6] gives "7 per cent and more" for the soluble tar in pyroligneous acid from air-dry beech wood. In American practice the soluble tar will run from 6 to 10 per cent of the pyroligneous acid; in laboratory distillations of hardwood pyroligneous acid is frequently obtained with 12 to 15 per cent of soluble tar. It might be expected that the amount of soluble tar would be greater when the concentration of acid or alcohol, or both, in the pyroligneous acid was greater, but there is no general rule to this effect. It is not even known whether the concentration of dissolved tar is limited by the amount of water-soluble pitch present or by the composition of the pyroligneous acid, although this could be indicated by the simple experiment of determining the solubility of settled tar in distilled or "tar free" pyroligneous acid.

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[4] Hawley, *Chem. & Met. Eng.* 25, 198 (1921).
[5] *Loc. cit.*, p. 57.
[6] *Loc. cit.*, p. 52.

Tar Distillation

On account of this solubility of alcohol and acid in the settled tar, the latter must be distilled in order to recover the valuable products contained in it. In cases where no special attempt is made to complete the distillation of the tar with the production of heavy oils and pitch, but where only the recovery of the alcohol and acetic acid is required, the settled tar is distilled with steam. When the tar is distilled with steam for this purpose the light oils are commonly distilled completely and also a varying amount of heavy oils, depending on the amount of steam used. The theory underlying this process is difficult to develop, since we are distilling with steam not merely an oil completely insoluble in water, which would be a simple case, but an oil containing in solution a substance, acetic acid, also soluble in water, and it is this acid soluble in both the oil and water which we are interested in distilling and separating. Apparently, however, the solubility of the steam in the acetic acid prevents the distillation of the latter along with the oils of the same boiling point, because although acetic has a boiling point of 118° C., yet it is not all removed from the tar even when all the oils boiling below 200° C. have been removed by the steam distillation.

Whatever may be the theory of this distilation the best conditions for carrying it out efficiently have been determined.[7] It has been found that when other conditions are constant a distillate more concentrated in acetic acid and a higher percentage recovery of acid are obtained by slower distillation. This is probably entirely a matter of obtaining equilibrium between the steam and the volatile constituents of the tar and might not be apparent in a tall and narrow still or below certain limits of speed. In a still containing 510 gallons of tar in a forty-inch layer and with speeds of steam averaging 25 and 50 gallons per hour, respectively, in two runs the slower speed gave 149 pounds of acetic acid in 219 gallons of water in 9 hours, 45 minutes, while the faster speed gave 139 pounds of acid in 273 gallons of water in 5 hours, 45 minutes.

The pressure of steam in the closed coils of the still or, in other words, the temperature of the tar while the steam is being blown through also has a very definite effect. In small laboratory apparatus two distillations were carried on under exactly the same conditions except that in one the temperature of the tar corresponded to 10 pounds steam pressure, in the other to 30 pounds. In the distillation at lower temperature a total volume of 446 cc distillate contained only 8.6 gr.

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[7] Hawley and Calderwood, *Jour. Ind. Eng. Chem.* 12, 684 (1920).

acid, while the higher temperature gave in 272 cc distillate 10.3 gr. acid.

There is no special problem in recovering the alcohol contained in the tar since on account of its low boiling point it is probably removed long before all the acid is recovered. The very likely possibility that the acid last removed from the tar by steam distillation consists largely of higher homologues of acetic acid has never been studied, although Fraps[8] identified some of the higher acids in the heavy tar oils.

Few details are available on the distillation of tar by direct fire heat for the production of light and heavy oils and pitch. As with other oils containing water in solution the first part of the distillation, while the water is distilling with the oils, must be carried on slowly and carefully to prevent foaming and "boiling over." After the water is all removed the distillation can be hastened without danger until near the finish, when, as the last of the heavy oils are removed, there is again danger from too rapid heating or carrying the distillation too far, since the pitch may be "coked." This "coking" of the pitch is apparently an exothermic reaction and may readily become uncontrollable. If after the distillation is finished the pitch is drawn off and exposed to the air while still very hot, there is also danger from its spontaneous ignition. Judd and Acree[9] have shown that in small scale distillation of tar, agitation of the charge with steam makes it possible to carry the distillation to the "hard pitch" stage without danger of coking the pitch.

When the tar is distilled by direct fire without the use of steam, the water which comes off during the first part of the distillation contains a large proportion of acetic acid but the higher fractions of oil, even those boiling well above 200° C., still contain some acid probably mostly acetic. Since there is no water collected with these oils the acid remains dissolved in them and can be recovered only by washing with water or a solution of alkali. In one of Judd and Acree's distillations with agitation by a jet of steam, where nearly one and one-half times as much water as oil was collected with the heavy oil, there was still 0.7 per cent acid in the oil.

The light oils have a dark color, especially after standing in the air, and a very pungent disagreeable odor. On redistilling, the color is lightened but not permanently. Neutralization with sodium carbonate before redistilling makes the color of the distilled product lighter and more permanent and also improves the odor. Preliminary experiments[10] have indicated that hydrogenation of the light oils gives an almost colorless product with a pleasant ketone odor, but no details are available on this treatment.

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[8] *Am. Chem. Jour.* *25*, 26.

[9] *Jour. Ind. Eng. Chem.* *9*, 276 (1917).

[10] Forest Products Laboratory "technical note," *Chem. & Met. Eng.* *16*, 708 (1917).

The heavy oils direct from the still are frequently the final market product, but they may require redistillation or neutralization or both. The fraction with boiling points between 195° and 230° C., is especially valuable for the production of "beechwood creosote" which is a specially refined part of the alkali soluble constituents boiling between 200° and 220° C., and probably consists mostly of guaiacol, creosol, homopyrocatechin dimethyl ether, and the xylenols, since these are the main known constituents of the oil having boiling points between these limits. The first three of these constituents probably occur in largest proportions in a well refined product, since they have the highest gravities and the refining process [11] is partly for the purpose of obtaining a high-gravity product.

The pitch usually requires no special refining process to make it a finished product. Its hardness is controlled by the point to which the separation of the oil is carried in the distillation Judd and Acree [12] note that when a hard pitch is prepared, the last small fraction of distillate solidified "to a jelly-like mass on account of the presence of paraffin."

Pyroligneous Acid Refining

The pyroligneous acid, partly separated from the tar by settling but still containing in solution certain non-volatile tar constituents, may be completely separated from tar by distillation. This distillation is practically nothing more than the separation of volatile from non-volatile material and no special problem of fractionation is encountered. A very small amount of oil distills over in this process and is separated from the aqueous distillate, but the "soluble tar" left behind in the still after all the aqueous distillate has been removed is practically free from oils. The soluble tar, however, contains in solution 7 to 10 per cent acetic acid which can be separated by the same process as is described for distilling settled tar for recovery of acetic acid (see p. 73).

The tar-free pyroligneous acid is next neutralized with lime for the formation of a non-volatile product of the acetic acid, so that the volatile wood alcohol can be separated by distillation. This neutralization, however, accomplishes much more than the formation of acetate of lime, since it is the cause of several complex reactions which affect the quality of the products subsequently separated. The details of these reactions due to neutralization have never been studied and it is only known that commercial practice has very definite but somewhat variable rules for deciding when the neutralization has been properly accomplished The addition of lime is accompanied by such marked color changes that the end point is readily determined by the color.[13]

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[11] U. S. Pat. No. 1,199,271.

[12] *Loc. cit.*

In a solution containing approximately 4.5 per cent methyl alcohol and 10 per cent acetic acid, there must be, in accordance with the equilibrium of the reversible reaction, a certain amount of methyl acetate. When the acetic

$$CH_3OH + CH_3COOH \rightleftarrows CH_3COOCH_3 + H_2O$$

acid is neutralized, the methyl acetate slowly hydrolyzes to methyl alcohol and acetic acid until equilibrium is again attained, the solution again becoming acid. If more lime is added the methyl acetate will finally be completely hydrolyzed, but more lime is not commonly added and the hydrolysis is so slow that methyl acetate is generally a prominent constituent of the distillate from the neutralized liquor.

A similar effect is due to the presence of formaldehyde in the pyroligneous acid. In slightly acid solution formaldehyde is stable, but when the solution is made slightly alkaline and heated it undergoes self-contained oxidation and reduction forming methyl alcohol and formic acid (see page 56). Here too a completely neutralized solution tends to become acid again, due to reactions started by the neutralization.

The most important and noticeable effect of neutralization is the formation of non-volatile organic compounds by polymerization, some of which are insoluble and help to form the sludge, others being soluble and thus becoming impurities in the acetate of lime. A few guesses have already been made that the insoluble polymerization products were mostly of the class of aldehyde resins and the soluble of the class of xylochinon, but these are only good guesses, and the organic part of the sludge and the organic impurities in the acetate are really of unknown composition. That the sludge contains organic material can be shown by boiling with hydrochloric acid to dissolve the lime and other inorganic constituents. A thick heavy oil is left which on cooling solidifies to a hard pitchy substance. The inorganic portion of the sludge probably consists of unburned calcium carbonate and other insoluble impurities in the lime.

The neutralized pyroligneous acid on distillation now yields the volatile constituents not fixed by the lime, consisting mainly of water, methyl alcohol, acetone, methyl acetate and allyl alcohol. By this distillation also some of the oils, especially the phenol ethers, which are apparently more soluble in the acid solution than in the neutral solution, are brought to notice by separating from the distillate. On further concentration of the alcohol constituents still more of these oils separate, probably on account of their greater solubility in methyl alcohol than in water. On account of the different solubility of these oils in different fractions of the distillate, it is advantageous to separate them continuously from the distillate, otherwise oils which are insoluble in some of the later parts of the distillate and can be separated from them may be redissolved if allowed to mix with the first part of the distillate in which they are more soluble.

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[13] Johlin [*Jour. Ind. Eng. Chem.* 7, 596 (1917)] says that this color change is largely due to traces of iron in the lime reacting with the di-methyl ether of pyrogallic acid or other phenol ethers.

The preparation of pure methyl alcohol from the crude concentrated wood alcohol is a more complicated process than a simple separation of various constituents according to boiling points. This is due to the facts that some of the constituents form constant boiling mixtures which can not be separated by distillation, that certain volatile bases, probably pyridines, require an acid washing for removal, and that oils soluble in the crude are not soluble in certain fractions and must be removed at the proper place.

According to Haywood[14] methyl alcohol and acetone form a constant boiling mixture consisting of 86.5 per cent by weight of acetone and 13.5 per cent methyl alcohol and boiling at 55.9° C. Bergstrom[15] found the mixture to consist of 90 per cent by weight of acetone and 10 per cent methyl alcohol, but he did not determine the boiling point. According to Ryland[16] methyl alcohol and methyl acetate form a constant boiling mixture consisting of 18 per cent methyl alcohol and 82 per cent methyl acetate, boiling at 53.5-54.5° C. He also states that methyl acetate and acetone form a constant boiling mixture, but the boiling points of the pure compounds are so close together that the composition of the constant boiling mixture could not be determined. From these figures it can be seen that methyl acetate and acetone can not be separated completely from methyl alcohol by distillation alone, but that methyl alcohol can be separated in pure state from the other constituents by losing a certain amount of methyl alcohol in the constant boiling mixtures.

It is not known whether a triple constant boiling mixture is formed, but if not, the results of distilling a mixture of these three constituents is much the same as if the mixture consisted of the three components, (1) methyl alcohol B.P. 66.5°, (2) constant boiling mixture of methyl acetate and alcohol with B.P. 53.5°, and (3) constant boiling mixture of acetone and alcohol with B.P. 54.5°. That this is the case is indicated by the fact that the first fractions on distillation have a specific gravity higher than the later fractions (methyl acetate sp. gr. 0.96, methyl alcohol and acetone sp. gr. both about 0.79). This is also indicated by the presence on the market of commercial products from wood alcohol refining, one containing 50-60 per cent methyl acetate,

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[14] *Jour. Phys. Chem.* 3, 349 (1899).

[15] *Bihang till Jernkontorets Annaler,* 1913.

[16] *Am. Chem. Jour.* 22, 384 (1899).

29 per cent acetone and the rest presumably methyl alcohol, the other containing 80 to 90 per cent acetone. The former of these products has a composition very near to that of 3 parts of low boiling mixture (2) and one part of mixture (3). The latter is almost the pure constant boiling mixture of acetone and methyl alcohol.

The separation of these constant boiling mixtures from methyl alcohol is difficult on account of the small differences in boiling points and this results in the production of large quantities of refined wood alcohol containing small amounts of acetone, since for many purposes small amounts of acetone are no disadvantage. The methyl acetate constant boiling mixture is more readily separated by distillation because there is less of it and it has a lower boiling point.

Many chemical methods for separating acetone from methyl alcohol have been suggested but they are apparently not as efficient as the separation by distillation, since none of them are used commercially. The formation of chloroacetone and subsequent separation by distillation is the favorite suggestion and a method based on the insolubility of acetone in caustic soda solution has also been described.[17]

The solution containing calcium acetate and organic impurities from which the alcohol constituents have been removed by distillation is now ready for the preparation of the acetate On account of the fact that calcium acetate is very soluble in water, and is more soluble in cold water than in hot, no rational method of concentration and crystallization has been developed, and instead evaporation and drying are the methods used for preparing the final acetate product. This method results in an acetate contaminated by organic impurities. Commercial acetates contain 80-83 per cent calcium acetate and this variation is probably due largely to the conditions of neutralization, although the exact effect of these conditions is not known. There is a certain amount of calcium formate also present. No data on the calcium formate content of American made samples are available, but Bergström [18] shows 2.3 per cent formic acid on two samples of acetate produced in Sweden from hardwoods. Just how much of the 17 to 20 per cent impurity is water of crystallization, hygroscopic water or inorganic impurity is unknown, although calcium acetate is supposed to crystallize with one molecule of water from hot solutions,[19] and this would give about 9 per cent water and 10 per cent organic impurity in an 81 per cent acetate.

Combinations of Steps in Refining

The simple refining process which has been discussed in some detail consists of numerous separate operations during which the main part of the crude distillate is repeatedly condensed and redistilled. This is an inefficient process from the standpoint of consumption of steam and condenser water and many methods are now in use for combining certain operations so that the vapors from one may be used as the heating medium for the other with corresponding economy in steam and condenser water. One suggested method is to use the heat in the vapors and gases as they come from the retort for a continuous refining process in which the products are separated by fractional condensation. The use of multiple effect evaporators is also becoming common for the distilling operations in which fractionation between volatile liquids is not required, such as the distillation of the crude pyroligneous and the evaporation of the acetate solution. The use of column stills on the neutralized pyroligneous acid for separating the alcohol in concentrated form in one operation is another combination of steps which increases efficiency in steam consumption.

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[17] U. S. Pat. No. 1,106,707.

[18] *Bihang till Jernkontorets Annaler*, 1912.

[19] Lumsden, *Jour. Chem. Soc. 81*, 355 (1902).

The first operation in the ordinary refining process, the distillation of the crude pyroligneous to remove the dissolved tar, requires a distillation of the entire watery distillate with immediate condensation, and nothing is accomplished except to prepare the pyroligneous acid for neutralization, after which it is immediately redistilled. If the soluble tar could be prevented from reaching the condenser by some device between the retort and the condenser, this first distillation could be avoided. Different methods for accomplishing this have been suggested and tried but there is only one plant in the United States where such an operation is even attempted and it is reported that only about half of the pyroligneous acid comes from the condenser free enough from tar so that it can be neutralized directly without redistillation.

The removal of soluble tar from the hot gases and vapors is not entirely a problem of fractional condensation because the soluble tar is *not volatile.* It must occur in the vapors in the form of a fog or mist which is so fine that it does not settle out in the short distance from the retort to the condenser. A partial cooling of the vapors until the first condensate is formed does not, therefore, cause a condensation of pitch (soluble tar) but a condensation of the highest boiling volatile constituents of the tar (heavy oils).[20] The condensation of a small part of the vapors may, however, be of assistance in the precipitation of the tar because the first drops of condensate are very likely to form on the suspended pitch particles and increase their size so that they more rapidly settle from the vapors. This is probably the principle upon which the tar separators work which cool the vapors until condensation just begins, and then pass the vapors through towers or columns where they are scrubbed with liquid tar. Klar[21] and Bergström and Wesslén[22] have described such tar separators but it is not known to what extent they are used in Europe or what quality of acetate can be made by direct neutralization of the pyroligneous acid passed through them.

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[20] In the vapors coming from a wood distillation retort at a temperature of say 200° C. everything is probably in the form of a true vapor except the actually non-volatile pitch. On cooling the first condensate consists of the highest boiling oils with boiling points around 270° C. If these oils were in vapor from below their boiling points only on account of the presence of saturated steam, water would condense along with them in the proportion required for their volatilization, but the steam is in superheated condition and there is also a considerable quantity of gas present and both the superheated steam and the gas carry the oil vapors the same as air or other inert gas carries water vapor below 100° C. It has been found that cooling the vapors to about 105° C. condenses most of the tar oils. (Hawley and Pier, *Chem. & Met. Eng.* 26, 1031, 1922.) The only oils which remain in vapor form above 100° C. are those which constitute the maximum amount that could be distilled with the amount of saturated steam present plus those carried in vapor form by the gas at that temperature.

Some preliminary experiments have been reported on another type of tar separator.[23] On a small retort a Cottrell precipitator was used with the idea that if the soluble tar existed in the vapors in the form of a fog it could be separated from the true vapors by electrostatic precipitation. This attempt was successful in stopping most of the pitch before it reached the condenser, but a small amount of soluble tar was found in the pyroligneous acid and the acetate made by direct neutralization was only 78 per cent pure calcium acetate in comparison with the 80 to 83 per cent obtained in practice by separating the tar by distillation. Either on account of poor insulation in the precipitator or because some of the soluble tar exists as vapor before condensation and polymerizes to non-volatile products afterward the results were not entirely satisfactory.

Two difficulties always encountered in any combination of steps in refining wood distillation products are caused by the continuous formation of "tar" throughout the process and by the separation of oils which should be removed from the products of a distillation before redistillation takes place. Apparently there are volatile products in the crude pyroligneous acid which slowly polymerize to non-volatile products—so slowly that they may not be removed in the first distillation but remain to deposit on evaporator tubes and in distilling columns during subsequent distillations. A continuous fractional condensation process of refining has been mentioned in which the heat of the vapors is sufficient for most of the refining process. After the vapors leave the tar separator they would be passed into milk of lime for separation of the acetic acid, and the temperature of the container would be maintained at such a point that a concentrated acetate solution would remain behind, while the alcohol vapors would pass over to a continuous column still where the water would be separated by fractional condensation and the concentrated alcohol would pass to a condenser. Such a process is perfectly possible and is ideal from the standpoint of fuel consumption, but there are difficulties to be overcome. The oils which get through the tar separator and would be removed from the pyroligneous acid before neutralization in the ordinary process now come in contact with the lime and probably form impurities in the acetate. Part of the oils would also remain uncondensed in the vapors from the acetate solution and would go to the alcohol still. Here most of them would probably be condensed with the water but some would carry through and contaminate the alcohol solution. Probably the greatest difficulty of a process of this kind, however, would lie in the non-condensible gas from the retort, which would carry through all the apparatus and finally pass out the condenser with the concentrated alcohol solution. We have already seen that there is a slight loss of alcohol in this gas even when it is separated by the retort condenser in the first step of the refining process. The loss would be very much greater in this case where the alcohol is much more concentrated and its vapor pressure is, therefore, much higher. In order to control this loss very efficient gas scrubbers would have to be used with large amounts of water for scrubbing, so that the gain in the fractional condensation process would probably be offset by the additional expense of recovering the alcohol from the wash water.

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[21] *Loc. cit.*, p. 185.
[22] Om Trakolning, p. 201.
[23] Hawley and Pier, *Chem. & Met. Eng.* 26, 1031 (1922).

It is hoped that this discussion of the chemical properties of wood, its decomposition by heat, the products of the decomposition and the processes of separating the valuable products, has been successful in bringing out the complexity of the subject, the small amount of detailed information available on important points and the opportunities for research on scientific details and on practical application.

PART II.

RESINOUS WOOD DISTILLATION.

Chapter I.

The Commercial Processes.

The resinous wood distillation industry is represented by two classes of processes so distinct in methods and in products that they will be treated separately. One of these is the destructive distillation process; the other, the extraction process or the "steam and solvent" process in which the resinous products are removed from the wood without decomposition and the wood remains behind unchanged. Many special and elaborate processes have been proposed for resinous wood distillation and some have operated on a commercial scale, but for some time the only commercial processes have belonged to one or the other of these two classes.

Destructive Distillation Process

The destructive distillation process is not standardized enough to make possible the description of a typical process, although the general principles are the same in all cases. The wood used is pitchy "lightwood" or old stumpwood from the longleaf pine, ordinary sawmill waste or green timber not containing sufficient pitch to make the process profitable. No other species of wood has been used in successful continued operation, although plants have been built and operated for some time using Norway pine and Douglas fir. The former has pitchy stumps and the latter forms occasional pitchy pieces of wood which can be picked out of the mill waste but in neither case can commercial quantities of wood be collected equal in quality to the longleaf pine wood.

The lightwood and stumpwood are selected to a certain extent in collection, not all the stumps or old dead wood on the cut-over lands or abandoned turpentine orchards being sufficiently pitchy. The stumps are removed from the ground by dynamite, the charge being placed so as to break the stump into several pieces as well as to loosen it from the ground. A little trimming with axe or saw then furnishes the wood in shape suitable for transportation to the plant. The lightwood is cut to straight four-foot lengths when possible but much of it is irregular in shape and size and is brought in in short pieces. The wood is in condition for distillation as delivered at the plant since no drying is required. The lightwood is air dry and the stumpwood, although part of it comes from beneath the ground, is much drier than green stumps. Only stumps from which the tree has been cut for at least ten years are used.

The distillation apparatus is of several different types; at one plant, vertical retorts are used; at several, horizontal cylindrical retorts of various sizes with charging and discharging by hand, and in other cases larger cylindrical or rectangular retorts, in which the wood is charged on cars as in the hardwood distillation process. In two plants the retorts are of concrete and the heating is accomplished by flues of large iron pipe inside the retort. In some cases also the charcoal is cooled inside the retort, although outside coolers are provided with all the retorts which charge the wood on cars. Only one cooler for one twenty-four-hour cooling period is required with resinous woods.

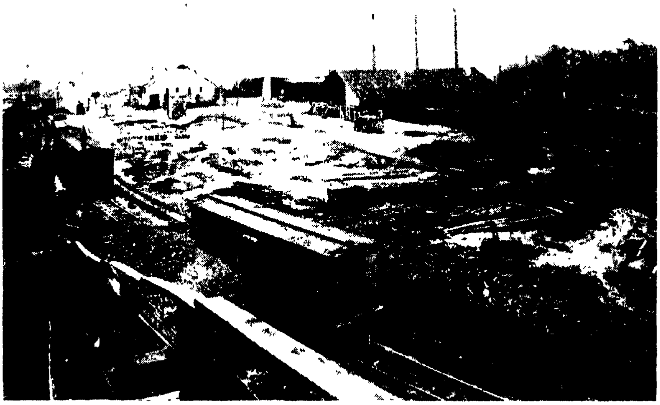

FIG. 13.—General View of Plant for Destructive Distillation of Resinous Wood.

The methods of heating and of taking off the products are also various. At most plants all the products are distilled and collected together without any attempt to obtain fractionation of the products from the retort. At other plants the first part of the distillation previous to the destructive stage is retarded and the maximum temperature kept low, until most of the volatile oil occurring as such in the wood is distilled over without much contamination by destructive distillation products. In this case two sets of condensers are used for the two stages in order to prevent contamination of the volatile oils by tar and pitch left in the condenser from the previous run. For some time a few plants have drawn off a part of the products from the bottom of the retort near the end of the distillation instead of distilling everything through the condenser. This material drawn from the bottom of the retort is naturally the least volatile portion of the products, the pitch. More recently a few retorts have been operated with the heat applied mostly at the sides and top, so that some of the high boiling oils could accumulate at the bottom along with the pitch and be drawn off as a heavy tar, thus obtaining a certain fractionation of products from the retort.

Fig. 14.—Retort House.

This type of retort was developed for small plants of one or two retorts only, with the idea that such small plants could not afford to install refining apparatus and in this way would produce partly refined products for shipment to central refining plants. Such small plants could be located near the wood supply and could operate in one place for several years without using up the wood in the immediate vicinity. In this way the products of distillation would be shipped instead of the wood, with a consequent saving on transportation charges. This plan has not yet been worked out on a large scale.

The condensation of the liquid products and separation of the fixed gas is carried out the same as in hardwood distillation. The liquid products consist of pyroligneous acid and crude tar the same as with hardwoods, but the tar, on account of the presence of resinous constituents of low gravity, floats on the pyroligneous acid. The main valuable products are found in the crude tar and the pyroligneous acid is usually a waste product. In only one plant has the acetate and alcohol been removed from the pyroligneous acid and this was profitable only on account of peculiar local conditions, including a cheap supply of fuel for the refining process.

After the separation of the crude tar by settling it is separated into various products by distillation and chemical treatment. In this refining process as in the distillation of the wood the processes are various. Few standardized products are made and many special products are prepared for the markets which have been developed by the individual plants. Pine tar is a fairly well standardized product and the commercial product is the residue left after various light oils have been removed from the crude tar by distillation. The crude tar is distilled in copper stills provided with closed coils and a steam jet and the distillation is carried on until the oil in the distillate reaches a certain gravity. The distilled oil with a gravity up to about 0.95 is separated for chemical treatment if refined turpentine and pine oil are to be obtained, or if refined turpentine alone, the oil up to about 0.895 is collected separately. This is treated with a solution of caustic soda for removal of some of the rosin oils and then distilled. The refined turpentine fraction sometimes includes all the oils with a gravity up to 0.87 or 0.875, or sometimes a separation is made of the light oils with boiling points below the turpentine range. The pine oil is separated so as to correspond fairly well with the standard steam distilled pine oil, except that the range of boiling points is usually wider in the destructive product. Various intermediate fractions are taken to prepare special products and a detailed typical process can not be described.

Pitch is obtained direct from the retorts in the plants where provision is made for drawing off a product from the bottom of the retorts during the last part of the distillation. This pitch needs no further treatment for market unless it is a little too hard or too soft, when it may be mixed with a little heavy oil or "boiled down" in a special pitch pan as the case may be. Pitch may also be obtained as a residue from the distillation of the tar, various heavy tar oils being obtained as a distillate in the process. This is not commonly done, however, since the process is difficult and the market for the products is not very good.

The caustic soda solution which has been used to treat the crude turpentine contains various constituents which can be reprecipitated by acidifying the solution, and this is sometimes done, using the pyroligneous acid for acidifying.

The lack of standardization in these pine tar products is in many ways a handicap to the industry, since the expansion of the markets is difficult when the same product can not be obtained from more than one or two plants. On the other hand, it is sometimes beneficial, since when the market is poor for one product it need not be separated but can be combined with other products. For instance, there might be times when the preparation of a refined turpentine would not be profitable, but the sale of the crude turpentine alone or with other fractions would save the situation.

The yields of various products can not be accurately given since there are such variations in the quality of wood used and in the composition of the products. The yields are sometimes stated in terms of total oil obtained per cord of wood used, and it is believed that about 80 gallons per cord is a fair average for this crude product.

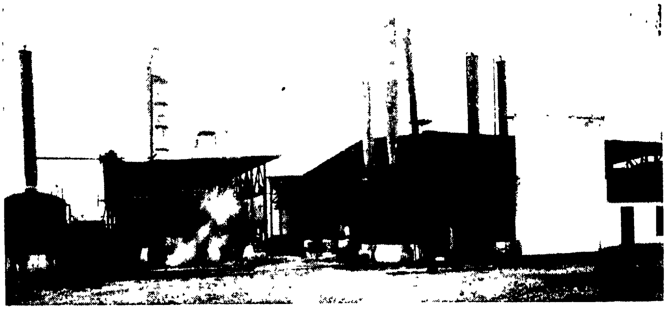

FIG. 15—Refinery.

Steam Distillation and Extraction Process

The raw material for this process is the same as that for destructive distillation and the same discussion on selection and collection applies, except that any piece small enough to go into the mouth of the "hog" or grinder is suitable for transportation to the plant. The wood after arrival at the plant is "hogged" into large irregular chips and then shredded into smaller and more uniform sizes. The hog and shredder are standard apparatus for comminuting fibrous material such as wood. The fine chips are carried by conveyor to bins at the top of the extractor building.

The removal of the valuable products from the wood takes place in a battery of cells or extractors and a part of the process is similar to the ordinary intermittent countercurrent, series extraction. Before the extraction with solvent, however, the crude turpentine is mostly removed from the wood by steam distillation, and after the extraction the solvent remaining on the chips is recovered by another steam distillation. All these operations are carried out in the same apparatus and each cell must, therefore, be provided with a steam jet, closed steam coils, inlets and outlets for the solvent, and separate condensers for the crude turpentine and the solvent. The extractors are vertical cylinders of various sizes holding from three to fourteen tons of wood and the greatest variation in design is in the discharging arrangements. In some cases the outlet for the finished chips is on the side near the bottom of the cylinder, in other cases the entire bottom of cell is removable so that the chips may fall out without restriction. The solvent is generally a special fraction of gasoline without the high-boiling portions which would contaminate the pine oil and make the solvent recovery difficult.

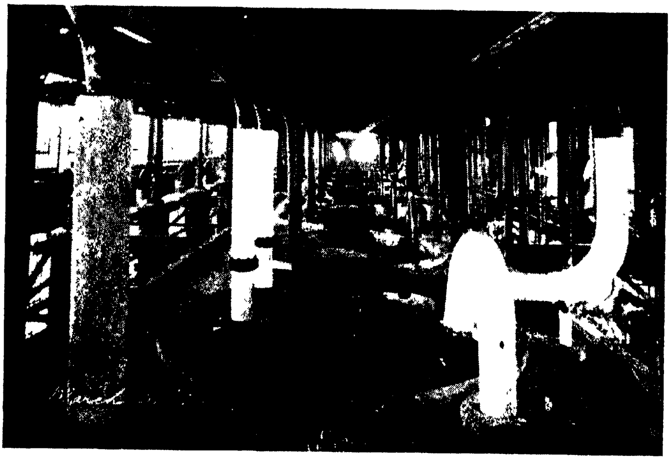

FIG. 16.—Interior of Extractor House.

The number of extractors in a battery varies at different plants from four to sixteen, but in every case the various operations of charging the fresh chips, steam distillation, extraction with solvent, solvent recovery and discharging the extracted chips take place in this order in each extractor and all the operations (except possibly the shortest ones of charging and discharging) are taking place in different parts of the battery at the same time. For instance, in an eight cell battery some one cell might always be charging or discharging, sometimes one and sometimes two steaming for crude turpentine, three extracting with solvent, and sometimes two and sometimes three steaming for solvent recovery.

The details of these operations vary at different plants; superheated steam may be used either for the solvent recovery or for both solvent recovery and turpentine distillation; the boiling of the solvent may be done by direct steam or by live steam; the solvent removed from the extractors during the boiling process may be returned to the cell or sent to storage; the speed and pressure at which the steam is blown into the charge of chips may vary.

In every case, however, the crude products of these operations for further separation and refining are the crude steam distilled turpentine and the solution of rosin in the solvent. The separation of the crude turpentine into refined turpentine and refined pine oil is accomplished by fractional distillation with steam, sometimes a little caustic soda being added to the crude turpentine before distillation. The distillation is controlled by the gravity of the distillate, the first fraction with gravity up to about 0.87 going into the refined turpentine, the second fraction up to about .91 being an intermediate part held over for redistillation, and the last fraction being refined pine oil. The residue of dark colored heavy oil is very small in quantity. The intermediate fraction is either held over until enough is obtained for a special distillation or else it is mixed with the next batch of crude turpentine.

The solution of rosin in the solvent also contains the pine oil not removed from the wood in the first steam distillation and the refining process is for the purpose of recovering the solvent for further use and separating pine oil and rosin in condition for market. This is also accomplished by fractional distillation, with closed steam coils during the first part of the process, and with live steam also during the latter part. There is a wide difference in boiling point and in gravity between the solvent and the pine oil, so that this separation is not difficult, and if some pine oil is distilled with the solvent it is not lost because it all goes back into the process again. Great care must be taken, however, to remove the last traces of pine oil from the rosin in order that the latter may be hard and brittle. After the pine oil is all removed the molten rosin is run into wooden vats and dipped or run into barrels.

There are two points about this process which must be carefully watched to prevent trouble, solvent loss, and contamination of the turpentine with the solvent. When working with large quantities of hot volatile solvent a few leaks or incomplete condensations result in a serious loss. It may also be noticed from the general description of the process that the same extractor is used for turpentine distillation and solution with gasoline solvent, and that a leak at the valve in the solvent connection to the extractor during the steam distillation would result in contamination of the turpentine with solvent.

At some plants there are two valves a short distance apart in the solvent connection to the extractors, and between the two is another valve opening to the air. When the solvent line is to be closed, both valves in the main line are shut, and the one between them is opened to the air.

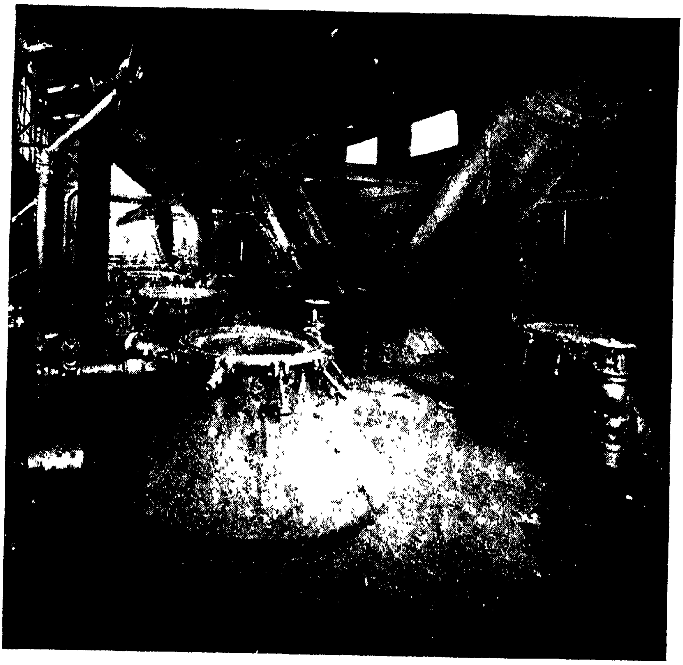

FIG. 17.—Tops of Extractors and Bottom of Chip Bins

The yields of products in this process vary considerably with the quality of the wood used and the completeness of the extraction, but it is believed that per cord of wood about 500 pounds of rosin, 14 gallons of turpentine and 6 gallons of pine oil are fair average figures.

Statistics

The latest statistics on resinous wood distillation are given in the Bureau of Census report, "Forest Products: 1919." Tables 17, 18, and 19 are taken from that report. Table 17 showing the number

TABLE 17.

SOFTWOODS CONSUMED IN DISTILLATION, BY STATES. 1919

State	Number of establishments	Quantity		Cost	
		Cords	Per cent distribution	Total	Average per cord
United States	25	256,108	100.00	$1,503,977	$6.22
Georgia	7	103,064	40.6	561,576	5.40
Florida	6	86,065	33.6	618,743	7.19
Alabama	3	41,416	16.2	264,01[illegible]	6.40
Louisiana	* 1	18,005	7.0	95,788	5.32
All other states........	† 5	6,748	2.6	52,958	7.85

* Includes 1 establishment distilling sawdust.

† Includes establishments distributed as follows: Michigan, 1, Mississippi, 1, North Carolina, 2; and Texas, 1.

and location of plants and the amount of wood consumed, does not make a distinction between destructive distillation and extraction plants, but a rough estimate of the relative size of the two processes can be obtained from the rosin figures in Table 18. This rosin must come only from the extraction plants, and at the rate of 1.8 barrels of rosin per cord of wood the amount of wood used by the extraction plants would be about 130,000 cords. The two branches of the resinous wood distillation industry were, therefore, about the same size in 1919. Two new extraction plants have been built since 1919, so that this branch is now probably larger than the destructive distillation branch.

Table 19 shows the actual holding capacity of the distillation apparatus in cords of wood, but this must not be taken as any measure of distillation capacity of the apparatus in cords per day, since the length of time the wood remains in the apparatus may vary widely. The division into retorts and ovens is also subject to criticism. In resinous wood distillation the distinction between retorts and ovens

TABLE 18

QUANTITY OF PRODUCTS FROM SOFTWOOD DISTILLATION: 1919

Kind	Quantity
Rosin ....barrels (280 pounds)	234,030
Turpentine ....gallons	1,534,333
Tar ....gallons	2,125,757
Tar oils .. ..gallons	581,042
Charcoal ....bushels	1,702,103
Wood creosote ....pounds	207,050

TABLE 19.
EQUIPMENT USED IN SOFTWOOD DISTILLATION.

State	Retorts		Ovens		Steam extractors		Aggregate capacity (cords)
	Number	Total capacity (cords)	Number	Total capacity (cords)	Number	Total capacity (cords)	
Alabama	20	10	..	..	60	150	160
Florida	18	30	11	70	40	320	420
Georgia	76	306	..	..	22	363	669
Louisiana	32	40	..	..	8	17	57
All other states *	50	78	..	..	2	20	98
Total	196	464	11	70	132	870	1,409

* Includes Michigan, Mississippi, North Carolina and Texas.

is not even so simple as in hardwood distillation, since there is a much wider variation in design of distillation apparatus in the former industry. About the only safe distinction between these two terms is to call hand-loaded apparatus "retorts" and car-loaded apparatus "ovens." If this line of division is made Table 19 is incorrect, since ovens of the same type as those used in Florida are found in Georgia also.

Statistics for foreign countries are lacking, although Sweden is known to have a considerable wood distillation industry in which softwood is largely used. The other countries around the Baltic Sea also produce large quantities of distillation products, mostly tar, from resinous woods. Much of this tar is made in tar kilns or "pits" without the recovery of other resinous products, and the name "Stockholm tar" applied to this product has become a common name for pine tar in general. Some time ago, "Russian turpentine," a crude destructively distilled wood turpentine, was a common article of commerce, being imported into England in large quantities.

Uses for Resinous Wood Distillation Products

Turpentine and rosin are very important chemical products with a large number of uses. The largest compilation of these uses is that given by the Leather and Paper Laboratory of the Bureau of Chemistry[1] which is reproduced here in complete form. It must be noted, however, that this list was prepared for the standard gum turpentine and rosin obtained from the live tree and that the wood distillation products may not be suitable in all cases. For instance, a turpentine from a destructive distillation process would not be used for pharmaceutical purposes (except possibly for disinfectants), for the finer grades of varnish, or as a raw material for chemical processes such as the manufacture of artificial camphor or terpin hydrate. In other cases where a different odor was objectionable the destructive distillation product might not be used. The steam distilled turpentine, however, is being used more and more like the gum turpentine, even in the finer pharmaceutical products.

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[1] *Naval Stores Review*, Apr. 28, 1917.

There are also some uses for gum rosin in which wood rosin has not yet been substituted on account of color or lower melting point.

These lists are very extensive and many of the uses mentioned are unimportant or are possibilities and not actual commercial operations but they show very strongly the widespread use and great importance of these raw materials. The largest and most important uses of turpentine are as a thinner and solvent for paints, varnishes, fillers, stains, polishes, etc. The largest and most important uses for rosin are as resinates (soaps, driers and size) in plastic compositions, and for rosin distillation products.

Steam distilled pine oil is a commercial product which is fairly new to commerce, and at first it was difficult to find a market for it, but soon many important uses were found for it and for some years it has commanded a higher price than turpentine. When the flotation process for ore concentration was first developed pine oil was found to be a very good flotation oil and for some time it has been considered almost a standard oil, the tests for new oils being comparisons with pine oil. Its pleasant odor, lack of irritating properties and high germicidal power have resulted in its use for antiseptics and disinfectants. It has very high solvent power for gums and resins so that many uses of this kind have developed. It is used in paints and varnishes to give the surface a "flat" effect. Its pleasant odor combined with solvent action has led to its use where a fairly cheap deodorizer is required in various oily or resinous compositions. It has recently been used as an ingredient in a denaturing mixture. It also has some chemical uses based on its high terpineol content. Destructively distilled pine oil does not have the finer uses where the pleasant odor is required but it is used largely for such purposes as flotation oils.

Pine tar has been an important commercial product for many years, but the original product was not made by wood distillation in closed vessels heated from the outside. It was made in tar kilns or tar pits somewhat after the manner in which charcoal was made without by-product recovery.[2] When the first pine tar was produced from closed retorts it was variable in quality and not like the standard "kiln tar." Two kinds of pine tar were, therefore, distinguished in the trade, kiln tar and retort tar, and the latter commanded a lower price. The retort tar gradually improved in quality and at one time brought a slightly higher price than the kiln tar. The two are now used practically interchangeably although they are quoted separately.

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[2] For a detailed discussion of the difference in methods of operating kilns for charcoal production and for tar production see Om Trakolning, p. 108.

Pine tar has a large number of minor uses but probably its largest single use is in the manufacture of cordage. Tarred rope and twine prepared with pine tar are standard cordage for many purposes. Another similar use for pine tar is in the impregnation of hemp fiber for the production of oakum. Tar is also used in paints, stains, and soaps, and for various pharmaceutical preparations such as ointments, cough remedies, hair tonics, and antiseptics.

There are various other products of the destructive distillation of pine wood called "tar oil," "pinewood creosote" or various special trade names, which are widely used for flotation oils and for other purposes similar to those mentioned for pine oil and pine tar.

Pinewood charcoal has the same uses as hardwood charcoal, although a greater proportion of it is probably used as domestic fuel on account of the local demands for it for this purpose.

Pinewood pyroligneous acid is not used in the manufacture of acetic acid and wood alcohol, so attempts have been made to sell it without any further refining. Several uses have been developed, such as for disinfectant, weed killer and raw material for pyrolignite of iron, but much of it is still a waste product.

USES OF TURPENTINE.

Compiled by the
Leather and Paper Laboratory of the Bureau of Chemistry.
Naval Stores Review, April 28, 1917.

Volatile thinner for paints, varnishes and wood fillers.

To accelerate oxidation of drying oils (as an ozonizer).

Solvent for waxes in shoe and leather polishes, floor polishes and furniture polishes.

Solvent for gums in lacquers and varnishes.

Ingredients of waterproof cements for leather, rubber, glass, metals, etc.

Solvent for waterproofing compositions.

Cleaner for removing paints and oils from fabrics.

Pharmaceutical purposes, including:

Disinfectants.
Liniments.
Medicated soaps.
Internal remedies.
Ointments.

Raw material for producing synthetic camphor and indirectly,

Celluloid.
Explosives.
Fireworks.
Medicines.

Raw material for producing terpineol and eucalyptol.

Raw material for producing terpinhydrate used in medicines.

Raw material for producing isoprene used in making synthetic rubber.

In the manufacture of sealing wax.

In glazing putty.

Ingredients of some printing inks.

In color-printing processes in lithography.

Lubricant in grinding and drilling glass.

As a moth repellant and in moth exterminators.

Constituent of insecticides.

For cleaning firearms (alone or in combination with other materials).

In laundry glosses.

In washing preparations.

In rubber substitutes.

In wood stains.

In stove polishes.

In modelling waxes and grafting waxes.

In belting greases.

In drawing crayons.

In the manufacture of patent leathers.

As a substitute for pine oil in flotation concentration of ores.

Solvent for rubber, caoutchouc and similar substances.

Used to prevent "bleeding" in the manufacture of cotton and woolen print goods.

Laboratory reagent as substitute for more expensive organic solvents.

Oxygen carrier in refining petroleum illuminating oils.

Colored turpentine, reagent for wood and cork in biological technic.

USES OF ROSIN.

Compiled by the
Leather and Paper Laboratory of the Bureau of Chemistry.
Naval Stores Review, May 12, 1917.

Manufacture of rosin soaps, including:

Laundry soaps and soap powders
Sizing for paper and paper board.

Paint driers. (Resinates of lead, manganese, cobalt and other metals, Japan driers.)
Axle grease.
Waterproofing compounds (insoluble rosin soaps).
Emulsifiable oils. (Lubricants for high speed tool work)
Leather dressings and shoe polishes.
Enamels used in ceramics (resinates of heavy metals).

Manufacture of certain varnishes and lacquers.
Manufacture of plastic compositions, including:

Sealing waxes
Cores for foundry work.
Rubber substitutes
Shoemaker's wax
Briquettes and fire kindlers
Artificial wood.
Composition for pattern making
Paper-mâché
Brewers' pitch
Roofing cement.
Grafting wax for trees
Cheap linoleum and oilcloth
In shoe bottom fillers.
Lutes.

Pharmaceutical purposes, including:

Ointments.
Plasters
Cerates.
Internal remedies (veterinary)
Disinfecting compounds

Making roofing materials.
Adulteration of ceresin and paraffin waxes.
Adulteration of beeswax and "artificial beeswax."
Adulteration of shellac and certain resins.
Manufacture of Venice turpentine substitute.
Flux for soldering and tin plating.
Dusting molds in foundries.
In dry batteries and electrical insulation (wiring).
Constituent of wood stains.
In belting grease.
On leather belts to prevent slipping (use inadvisable).
On violin bows.
For setting bristles in hair brushes.
Constituent of insect powders.
For the manufacture of "artificial copal."
In steel hardening.
Constituent for enamel for brick walls.

Coating for match splints.

Constituent for some floor waxes and polishes.

In wax tapers.

Hardening tallow candles.

In stamping powders.

Sizing for wood-pulp wall board.

In waterproofing compositions for paper, card board and fabrics.

Paper hangers' size.

Making imitation Burgundy pitch.

Manufacture of munitions (filling vacant space in shrapnel).

Manufacture of sticky fly-paper.

Constituent of sweeping compounds.

Waterproofing wooden fence posts.

In mixtures to protect trees from climbing insects.

Constituent of printing inks.

In cements (for glass, etc.)

For caulking ships.

In sulphite-waste utilization (Trippe process.)

In the manufacture of condensation products.

As a raw material for producing certain chemicals (benzene derivatives).

In the manufacture of carborundum and calcium carbide (using sawdust and refuse wood chips with residues from the manufacture of turpentine and rosin).

In destructive distillation to produce:

Rosin oil and rosin oil products used in:

Cements.
Lubricants (oils and axle grease.)
Printing inks.
Adulterating linseed oil.
Brewers' pitch.
Varnishes.
Rubber substitutes.
Funnel paints for yachts.
Flotation concentration of ore.
Mixtures to protect trees from climbing insects.
Shingle stains.
Waterproofing textiles and cordage.
Manufacture of lamp black for lithographic purposes.
Soap making.
Leather dressings and shoe polishes.
Sweeping compounds.
Adulterating olive oil and castor oil.

Rosin spirits used in:

Illuminants.
Turpentine substitutes.
Cheap varnishes.

Acetic acid used for making:

Acetate of lime (source of acetone).
Acetate of iron (mordant and mineral dye).
Acetate of alumina (waterproofing cloth).

Pitch used for:

Cobblers' wax.
Preserving cordage and nets.
Roofing felts and waterproofing papers
Bituminous paints.
Binder in briquettes.
Caulking ships.
Cements, lutes.
Electrical insulations (dry batteries, wiring, etc.).
Plastics for pattern making
Grafting wax for trees.
Paving materials
Steel hardening compositions
Waterproof masonry

Chapter II.

The Raw Material.

The difference in chemical composition between hardwoods and softwoods has been shown in Table 1, but this difference is only between the common, average wood for each group and does not indicate the difference between the raw materials used in the two industries. This is for the reason that the resinous wood distillation industry uses only wood selected for its high resin content. The normal resin content of certain resinous wood is shown in the ether soluble figures of Table 4, longleaf pine and western yellow pine being the most resinous. Resin is not evenly distributed in the tree, however, and certain portions may contain very much more resin than the average. The sapwood contains very little resin, while the heartwood of the stump and butt log is very resinous, pitchy or "fat." There are also frequent high concentrations of resin in the upper parts of the tree, especially at the junction of the limbs with the trunk.[1] The practice of turpentining the longleaf pine tree also frequently causes accumulation of resin in the wood just underneath the turpentine "face." The detailed mechanism by which this resin is concentrated in certain places is not clearly understood.

From this point forward the discussion is limited to the longleaf pine tree unless specific mention is made of another species. This is for the reason that this species is the only one used commercially and about which there is any detailed information. The presence on old cut-over lands or in abandoned turpentine orchards of large quantities of loose pitchy wood locally called "lightwood," * "fat wood" or

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[1] Lightwood, Cut-Over Lands and the Naval Stores Industry, *Naval Stores Review*, Special Number, 1921.

* Lightwood is not only applied to this loose resinous wood but also sometimes to the pitchy wood from stumps or in lumber. This word is frequently pronounced "lightered" and an occasional variant of the name is "lighterwood." The name probably originated in the common use of this pitchy wood for torches since it certainly could not develop from either the color or the weight of the wood. "Pine knots" is the name commonly applied to the peculiar conical shaped piece of resinous wood which comes from the junction of the limbs and the trunk. To distinguish the stumps from the pitchy wood occurring loose on the surface of the ground the latter is frequently called "top wood." Lightwood has long been an important material in the "piney woods" region of the South through its use for torches, and for domestic and industrial fuel. It was long used as fuel for railroad engines and only recently the queerly shaped stack of the wood burning locomotives could be seen in many places in the South. Lightwood is still commonly used as fuel for the steam skidders in logging operations on account of its high fuel value and because the ordinary green wood which might be cut for the purpose could not develop sufficient steam when burned in the ordinary small fire box.

"pine knots" and the high resin content of old pine stumps have led to the belief that longleaf pine wood increases in resin content after the tree dies or is cut. It is possible, however, to account for this very pitchy wood by considering it a residue left after the decay of the sapwood and the less resinous portions of the heartwood, the residue being protected from decay by its high resin content.

In a study of the utilization of wood waste made by Arthur D. Little, Inc., for the Great Southern Lumber Co., all the stumps on each of several one acre plots were carefully measured for the proportional areas of bark, sapwood, decayed wood, ordinary heartwood, and "lightwood" on the freshly cut surfaces. Samples of the wood from average stumps, about one-eighth of the total number, were then taken by collecting the sawdust from a cut halfway across the stump about 1½ inches below the top. Determinations of the resin content of these samples corresponded very closely with values computed from the areas of the different kinds of wood, when the following resin contents were assumed (see table p. 105).

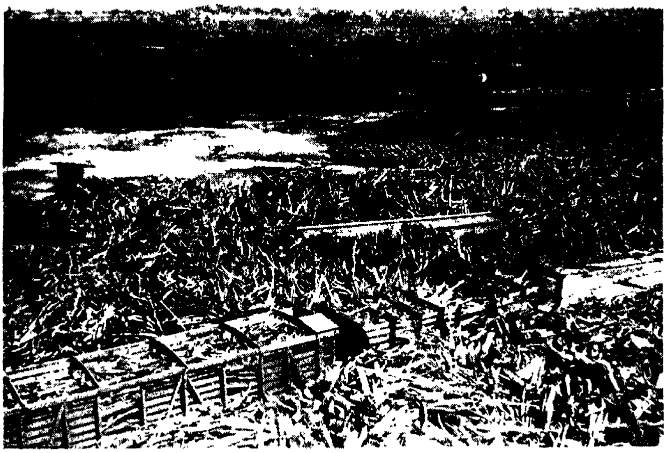

FIG. 18.—Wood Yard and Rosin Storage

If from these assumed figures the resin content of the stumps was computed after the bark and sapwood had been removed by decay, the average computed value was fully as high as that of the average old

Bark	2 per cent
Sapwood	3 " "
Decayed wood	0 " "
Ordinary heartwood	19 " "
Lightwood	43 " "

stump. This shows that it is unnecessary to assume any increase of resin in the stump after the tree is cut in order to account for the high resin content of old stumps.

It is just possible that in the case of decaying wood, where the resin content is high but not quite high enough to prevent decay, the resin diffuses forward in front of the decaying process until the concentration is high enough to prevent further decay. This hypothesis is the result of the observation of peculiar bands of especially resinous wood near decaying surfaces and has little confirmatory evidence.

Composition of the Resin *

The composition of the oleoresin obtained by cutting into the live sapwood of a longleaf pine tree is fairly well known, since it is composed of two well-known chemical raw materials, turpentine and rosin. The turpentine portion consists practically entirely of alpha and beta pinenes. The composition of the rosin can not be stated so definitely but it is supposed to consist mainly of abietic acid with a small portion of alkali insoluble "resenes" of unknown composition. This does not tell the whole story, however, since rosin varies considerably in color and in the chemical constants commonly used in reporting the results of its examination such as acid number, ester number and iodine number which vary over a considerable range.

The composition of resin occurring in lightwood is different from that of the oleoresin as first formed in the resin cells. This was a fact not realized until the volatile oils in the wood were obtained in uncontaminated condition and in commercial quantities by the steam

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* In order to avoid confusion the nomenclature to be used in this discussion is given here together with other terms commonly used for the same materials.

"Resin" is applied only to that resinous material occurring in the wood. "Pitch" is a common synonym.

"Oleoresin" is applied only to the resinous material formed as a result of a wound in the sapwood—the fresh pathological secretion of the resin cells. The turpentine operators call this "gum" or "dip" and some writers call it "turpentine" or "crude turpentine."

This distinction between resin and oleoresin is not advocated for general use but the other nomenclature is justified by common usage.

"Turpentine" is applied only to the volatile part of the oleoresin or to a similar material from the resin. This is commonly called "spirits" or "spirits turpentine" or plain "turps." Translators from the French frequently call it "essence" from the French word for turpentine.

"Rosin" is applied only to the non-volatile portion of the oleoresin or to a similar material from the resin. "Colophony" is the literary term for the same material. It is often called "resin" by the fastidious who do not like the rough, vulgar sound of correct name. This causes confusion on account of the proper use of resin for another material. Rosin may be classed under the general term of resins but it is not "resin."

distillation process introduced about 1903. This is shown by the description in Forest Service Circular No. 9 (1895) of a method for determining turpentine in resinous wood which consisted in volatilizing the turpentine in a current of warm air, burning it in a combustion tube and computing the amount of turpentine from the carbon dioxide formed. It was not known at that time that any other volatile compounds were present beside terpenes with the formula $C_{10}H_{16}$. It has since been found that not only are there volatile oils other than turpentine present in the resin in lightwood, but that the composition of the true turpentine constituents (terpenes) is different. The manufacturers of steam distilled turpentine had found that there was an oil obtained by steam distillation of the wood which had a higher boiling point and higher gravity than turpentine. This oil was called "pine oil."[1] Teeple[2] and Toch[3] had identified single constituents of this oil but it was not until Schimmel and Company[4] studied it that all its main constituents were determined. They reported the following eleven constituents: alpha pinene, beta pinene, dipentene, limonene, camphene, cineol, alpha terpineol, borneol, fenchyl alcohol, camphor and methyl chavicol. Since the first six of these have boiling points below 180° they should be considered turpentine constituents which were found in the pine oil due to incomplete separation. The other five all have boiling points above 200° C. and are the true pine oil constituents. Alpha terpineol is probably the main constituent of pine oil and it has been shown[5] that alpha pinene and dipentene are the main constituents of the turpentine.

The differences between the wood rosin and the gum rosin can not be stated so definitely as those between wood turpentine and gum turpentine, since the actual chemical composition of the rosins is not so well known but the variation in certain chemical and physical constants can be given. In color the wood rosin is of medium grade, E or F on the rosin scale, but with a reddish tint not found in gum rosins. The exact cause of this difference is not known. Wood rosin also has a lower melting point than the average gum rosin. Palmer says on this point: "The cause of the lower melting point is the presence of a small amount of material which appears to be in the transition stage between oil and resin . . . of such high boiling point that it can not be separated from the rosin by distillation. . . . It is doubtful if wood rosins of the lower grades can ever be produced which will melt much above 56° C. compared to the average of 62° C. for gum rosins. The normal melting point of standard wood rosin now on the market is from 53° C. to 55° C.[6] Compare this uniformity with gum rosins whose melting points vary from 50° to 70° C." Palmer also gives the saponification value of wood rosin as 158 to 160, while gum rosin varies from 155 to 175, but with an average higher than the wood rosin. The unsaponifiable matter in wood rosin is less than 5 per cent, while many gum rosins have a higher figure. The products of destructive distillation of wood rosin differ very little from those from gum rosin. The yields are fully as great but the proportion of the different fractions are somewhat different. The evidence at hand now seems to indicate that the abietic acid in wood rosin is an isomeric form of the same body in gum rosin, one indication of which is seen in its lower solubility in such solvents as benzol, petroleum, naphtha, alcohol, etc.[7]

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[1] "Pine oil" is the term which has been much used as an English equivalent for the German word "kienol" This German word is really the equivalent of our "destructively distilled wood turpentine" and after the new commercial product of steam distillation was called pine oil much confusion resulted. This later use of "pine oil" has rapidly expanded in this country and is now in common usage in market quotations and technical literature.

[2] *Jour. Ind. Eng Chem. 6,* 722.

[3] *Jour. Am. Chem. Soc. 30,* 412 (1905).

[4] *Semi-Annual Reports,* Apr., 1910.

[5] Forest Service Bull. 109, p. 53.

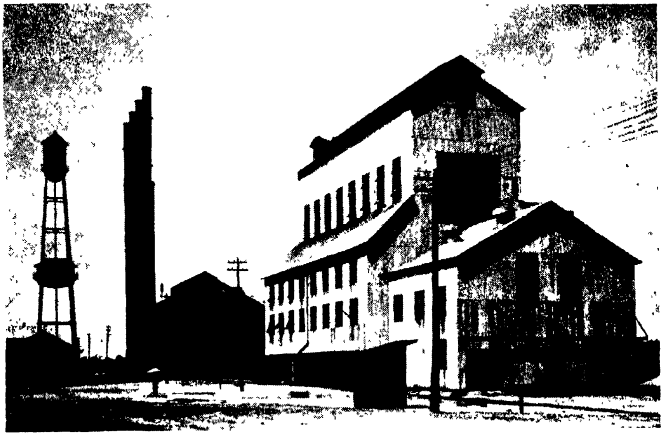

FIG. 19--Extractor House and Power House.

It is difficult to account for this great difference in the composition between the volatile oils from the fresh oleoresin and those from the resin in the old wood. At first an attempt at an explanation was made by suggesting that the process of distilling the oils from the wood transformed the two constituents of the original turpentine into the nine new compounds but, with the possible exception of the transformation of alpha pinene into dipentene this was obviously an impossibility, since steam at low pressures and in short periods could not accomplish such great changes in composition. It has also been shown[8] that increased steam temperature has no effect on the proportion of pine oil and that distillation at 50 pounds steam pressure is without effect in transforming pinene into dipentene. It is, therefore, necessary to conclude that all these constituents of the volatile oil exist as such in the resin and are formed by gradual oxidation, hydrolysis or rearrangement of the alpha and beta pinenes in the original fresh oleoresin. That the change is slow and progressive is indicated by the fact that steam distilled total volatile oil from green, fresh, sawmill waste consisting mostly of slabs (sapwood) contains less pine oil than that from old stumpwood (heartwood) and that no dipentene was detected in the former.[9] It has also been found that the proportion of pine oil is less in the outside (young) portion of a log than in the inside (old) portion.[10]

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[6] *Naval Stores Review*, Special Number, 1921, p. 262. In a recent private communication Mr. Palmer states that the melting point of certain commercial wood rosins is now much higher than 56° C.

[7] These statements are all taken from Palmer, *loc. cit.*

Accurate figures on the ratio of volatile oil to rosin in the resin of the old wood are not available, but the best estimate gives about 20 per cent of volatile oil. This is in comparison with about 25 per cent volatile oil in the fresh oleoresin. The proportion of heavy oil in the volatile oil of the resin may vary from 10 per cent in green wood to 50 per cent in old stumps.

It has been shown in Chapter II of Part I that the yields of methyl alcohol and acetic acid from the distillation of softwoods are much lower than those from hardwoods. Aside from the variation in the composition of the tar due to the presence of resin, it is not known what differences may exist in the other products. It is not even known whether a non-resinous softwood gives a tar just like a hardwood tar, but from general appearances there is no difference. It has been reported[11] that redwood, a softwood with very little resin, gives a tar with high proportions of phenol and cresol, but no details have been given and it is believed that this is not the case with other softwoods. The only explanation of this difference is in the high water soluble content of redwood (See Table 4) since no other difference in composition is noticeable from the chemical analysis.

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[8] Forest Service Bull 105, p. 25

[9] Forest Service Bull. 105, p 43.

[10] Forest Service Bull 109, p. 22.

[11] U. S. Pat 1,365,407

Chapter III.

The Decomposition of Resinous Wood by Heat.

The decomposition of softwood by heat follows much the same course as the complicated reaction described for hardwood and, in the case of the highly resinous wood used commercially, the process is further complicated by the presence of considerable quantities of resin and the products from the wood are mixed with the distillation products of the resin. Knowing the properties of the constituents of the resin it is possible to describe the manner in which the mixture of wood and resin distils when subjected to gradually increasing temperatures.

The volatile oils distil mostly below the temperature at which wood begins to decompose strongly, say 250° C., so that it might be a fairly simple matter to distil these oils before the wood distils and, therefore, obtain them free from contamination by the decomposition products of the wood. This seems even more readily possible when we consider that these volatile oils in the presence of steam distil below 100° C., and if there is enough water in the wood to furnish the steam they might be completely distilled below 100° C. There are, however, some difficulties in the way of accomplishing this result. We have seen that wood is a poor conductor of heat, and when distilling large charges of wood the temperature gradient between the outside and inside of a charge is very rapid, so that slow and careful heating would be required to obtain the distillation of the volatile oils without decomposing a part of the wood. The presence of the rosin causes even more difficulty since it begins to decompose at even lower temperatures than the wood and since it lowers the vapor pressure of the turpentine. Accurate figures are not available for the minimum temperature of the decomposition of rosin, but in the steam distillation of wood it has been shown[1] that there is some contamination of the turpentine when distilled from the wood at 75 pounds steam pressure (160° C.) and that this is probably due to the beginning of decomposition of the rosin. The decomposition at this temperature is only slight and it is believed that even up to 200° C. the volatile products given off by rosin are still small in amount. Higher than this, however, the rosin begins to decompose rapidly and 200° C. is usually considered the highest temperature to which resinous wood can be heated without serious contamination of the turpentine by rosin decomposition products.

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[1] Forest Service Bull 109, p 25

It would be expected that considerable turpentine would be driven off from resinous wood at temperatures near 100° C., since a mixture of water and turpentine will boil below this temperature but it is not until about 160° C. is reached that much distillate is actually obtained. The reason for this is probably that the water and the oil are not in contact in the wood and it is not until the resin becomes a thin fluid with the heat and begins to flow in the wood that much distillation can take place. That such a flow does take place is shown by the fact that with rich wood and carefully controlled temperature considerable quantities of rosin can be drawn off from the bottom of the retort after the temperature has been held at 180 to 200° C. for some time. If the temperature is carefully controlled all the turpentine and part of the pine oil can be distilled off before the rosin begins to decompose. Then as the temperature is raised the rosin begins to distil rapidly, and finally the distillation point of the wood is reached. Commonly, however, these separate stages are not readily distinguished, and a mixture of volatile oils, rosin products and wood distillates may come over together from the start.

The presence of the resin makes it possible to obtain a liquid product from the bottom of the retort by drawing it off at some stage in the distillation instead of distilling it off through the condenser. It was noted above that with proper care an only slightly decomposed rosin could be drawn off during the first stages of the distillation. If the retort is tapped at a later stage or if the temperature is not controlled, a tar may be drawn off. If this tar is allowed to remain until the last stages of the process, a hard pitch may be drawn off.

Before discussing the products of distillation it will be necessary to state what little is known about the composition of rosin distillation products, since rosin is such a large part of the raw material. Rosin has been distilled commercially for many years and many publications have been made on the subject but yet little is known on the actual composition of the products. A few indefinite compounds have been identified or at least have been named, but not even a table giving percentages and boiling points or specific gravity of the oils has been published. The usual terms in which the products are described are the trade terms, such as "rosin spirits," "kidney oil" and "blue oil." [2] It is known in a general way that on distillation rosin furnishes a very complex series of oils with boiling points all the way from 50° to 370° C., thus overlapping completely the boiling range of wood tar oils, of turpentine and pine oil. The oils are only partly soluble in or polymerized by alkali and this characateristic can be varied largely by the

[2] Shuey, *Naval Stores Review*, Special Number, p. 233 (1921).

conditions of distillation.* This is about all that can be said on rosin oils and indeed is all that is necessary for the further discussion.

The process in which the turpentine and pine oil are distilled first at low controlled temperatures will not be discussed further since this is not a common commercial practice, but instead the more common process of distilling in which all the products come off more or less mingled and are collected together for further refining. The discussion will be further limited to the process in which all the products are distilled and none is drawn off the bottom of the retort. The total oily distillate will then consist of the turpentine and pine oil originally present in the wood, together with the wood tar and the rosin oils.

There is a difference of opinion without data on either side in regard to the effect of different systems of distillation on the yield, composition and value of the oily distillate. It is commonly believed that certain retorts with poorly arranged heating flues may "burn up" the distillate giving low yields and poor quality products, but from what we have seen of the decomposition and distillation of the different constituents of the raw material, volatile oils, rosin, and wood fiber, it is difficult to understand how there can be any noticeable diminution in yields of total oil even with considerable superheating during the distillation process.

To take a concrete instance, suppose the maximum temperature to which the bottom of the retort was heated was 500° C., what would be expected in the way of loss of total oily distillate? Only a small part of the distillate would necessarily be subjected to a temperature anywhere near as high as this, and even this small part would be decomposed into nonliquid products such as coke and gas only to a small extent at this temperature. Suppose 10 per cent of the products are subjected to the maximum temperature and thereby 10 per cent of this portion are decomposed into coke and gas, the total loss would be only 1 per cent or a practically negligible quantity. With any reasonable skill in designing the heating system of a retort and reasonable care in operation it should be possible to keep the maximum temperature below 500° C. and obtain full *yields* of products.

There is more to be said in regard to *quality* of products, however. It has been stated that the composition of the distillation products of rosin varied with the condition of distillation and that unnecessarily high temperatures would give more decomposition of the original rosin and a product more like "second" or "third run" oils. It is possible, therefore, that the composition of that part of the total distillate which comes from the rosin may be varied by the amount of superheating during the distillation. So little is known of the detailed requirements of composition for these distillation products that it can not be foretold whether such a superheating would cause an improvement of quality or otherwise.

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* This is for the reason that rosin is slightly volatile at the temperature of its destructive distillation and, therefore, varying quantities of undecomposed rosin are vaporized with the volatile decomposition products. If rosin is carefully distilled in vacuo a very large proportion can be obtained as solid undecomposed rosin, if distilled slowly at atmospheric pressure a considerably smaller proportion of unchanged rosin is obtained and if distilled rapidly a still smaller proportion. In practice frequently the unchanged rosin is not wanted and the "first run" oil is redistilled in order to decompose it further; the "second run," "third run," etc., oils resulting are thinner and contain less "rosin acids." We have often wondered why a single distillation under pressure might not accomplish the same results as repeated distillations at atmospheric pressure.

The effect of slight superheating on the composition of the pine oil constituents is not known, but it is believed that the effect is not serious. It is known, however, that at temperatures above 250° C. pinene may be transformed into dipentene. That this does take place to a certain extent in commercial wood distillation processes has been shown by the composition of the refined wood turpentine. One wood turpentine contained about 40 per cent dipentene instead of the 10 per cent normally present.[3] This change of part of the pinene into dipentene does not result in any considerable reduction in value, however.

Softwoods are somewhat different from hardwoods in the distribution of methoxyl groups in the distillation products.[4] There is less methoxyl in the pyroligneous acid, corresponding to the lower yield of methyl alcohol. There is also less methoxyl in the dissolved tar and more in the settled tar from softwoods. The effect of treating the softwood with sodium carbonate before distillation is much the same as in the case of oak: the methoxyl in the pyroligneous acid is increased and that in the dissolved tar, the charcoal, and the gas is decreased. With the softwood, however, the methoxyl in the settled tar is decreased very considerably by the sodium carbonate.

Yields of Products

The question of yields of turpentine, pine oil, tar oils, tar and pitch or, in short, of total oily products is one that is apparently not properly comprehended and that is the cause of many mistakes and failures. It has already been stated that the yields depend almost entirely on the amount of resin in the wood distilled and that this is a very variable factor. Ordinary unselected sawmill waste or green limbs from longleaf pine may contain only about 5 per cent resin and give tar products only a little greater in quantity and a little different in quality than are obtained from hardwood, say 27 gal. per ton of a black tar with about 40 per cent pitch A poor grade of lightwood may contain 15 per cent resin and yield per ton 46 gal of total oils, including a tar with a more brownish color and less pitch, while a very rich lightwood or stumpwood with 30 per cent resin might yield 78 gal. of oil containing a tar of golden brown color and very little pitch. The increase in yields with increasing resin content is due to the much higher proportion of oils from resin than from wood, while the change in quality is due to the increasing proportion of resin products with different characteristics from the wood tar. These yield figures are computed on a basis of a yield of 7 per cent tar and oils from the wood fiber 80 per cent from the rosin and 100 per cent from the volatile oils. The "ton" is also considered as a ton of water-free wood and the resin is assumed to consist of 80 per cent rosin and 20 per cent volatile oils.

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[3] Forest Service Bull. No 105, p 52

[4] Hawley and Aiyar, *Jour Ind. & Eng Chem.* 14, 1055 (1922).

When the corresponding yields are figured on a cord basis the variation in the yields from the different qualities of wood are even greater, due to the fact that as the resin content of the wood increases its weight per cord also increases. For instance, ordinary longleaf pinewood with 15 per cent moisture and 5 per cent resin weighs about 42.5 pounds per cu. ft. (see Table 11) and an increase of resin content to 15 per cent should increase the weight per cu. ft. by an equivalent amount $\frac{(42.5}{(1.15} \times (15 - 5) = 3.7$), assuming that the additional resin does not swell the volume of the wood. A cord of wood with 15 per cent resin would, therefore, weigh $(42.5 + 3.7)\ 80 = 3606$ lbs., and figuring in the same way a cord of wood with 30 per cent resin would weigh 4136 lbs. Since a cord of ordinary wood with 15 per cent moisture is equivalent to $\frac{3400}{1.15 \times 2000} = 1.48$ dry tons, it will yield $1.48 \times 27 = 40$ gals of oil per cord. Figuring in the same way, the wood with 15 per cent resin and weighing 3606 lbs. per cord will yield 75 gal. and the wood with 30 per cent resin and weighing 4136 lbs. per cord will yield 152 gal. of total oil.

These figures are believed to represent very well the commercial yields obtained from wood with such resin contents, and at any rate they are good examples of the variation in yields due to difference in quality of the wood. They show why it might be preferable to pay a high price for a very rich wood rather than to distil ordinary sawmill waste which could be obtained very cheaply. The tar obtained from poor grade wood is also so near like hardwood tar in composition that it is difficult to find uses for it.

It is a common practice to report yields of oils from a particular process or apparatus without any statement as to the quality of wood used, but with the inference that the high yields are due to the process, when the quality of wood and not the process may have been responsible for the favorable results. Even when conscientiously testing a new process for distilling resinous wood it is very easy to be deceived by the unconscious selection of very rich wood for the trial runs. No publication has been made on the destructive distillation of resinous wood and the author has never seen a private report on this subject in which yield figures were accompanied by determinations of the resin content of the wood used.

The charcoal obtained from resinous wood has much the same composition as that from hardwood except that it may contain a certain amount of the "coke" from the distillation of the rosin in the wood. The rosin which does not flow from the wood during the first part of the distillation finishes its decomposition while retained in the wood (or charcoal) and naturally leaves its distillation residue mixed with the charcoal. This tends to make a denser charcoal than that obtained from softwood with little resin.

The gas from resinous wood distillation is also affected by the presence of "rosin gas" which gives it a much higher illuminating power than the hardwood gas. Like the hardwood gas, however, it is used only for heating purposes at the plant.

Chapter IV.

Refining Destruction Distillation Products.

When the total distillate is condensed together the tar does not commonly settle to the bottom as in the case of hardwood distillation, but on account of the low gravity oils produced from the resin the total oily distillate is lighter than the pyroligneous acid and floats. On distilling a pine wood with very little pitch in it the tar would probably sink, but in any commercial plant distilling wood that is pitchy enough to make a profitable operation the total oils always float. Figure 19 gives the boiling point and specific gravity curves for a typical total distillate from a wood containing about 23 per cent resin. There is no standard method for the separation of such a mixture into commercial products since different commercial plants have developed special products for their customers or vary the products to suit the demands of the trade. Sometimes the total oil as separated from the pyroligneous acid is sold without further refining. A typical refining operation will be described, however, as an example of a simple process with a small number of products.

The Oil

The oil whose composition is indicated in Figure 20 is distilled with steam for the separation of the oils with boiling points up to about 190° C. or the corresponding gravity of about 0.92. Since the principles underlying distillation of an oil with steam are not generally understood and since these principles are frequently applied in resinous wood distillation, a short explanation will be given here. When a single liquid like water or a mixture of two miscible liquids like water and alcohol is heated it begins to boil when the vapor pressure of the liquid equals the atmospheric pressure. The physico-chemical law governing steam distillation states that when two non-miscible (mutually insoluble) liquids like oil and water are heated while kept in equilibrium (well stirred) the mixture will begin to boil when the *sum* of the vapor pressures of the two constituents is equal to atmospheric pressure. This means that the mixture will boil at a temperature lower than the ordinary boiling point of either the oil or the water. Advantage is often taken of this principle to distil oils with boiling points above those readily reached by pressure steam. Since the distillation of a mixture of oil and water is not convenient on account of still capacity and tendency to bump and froth, the same thing is accomplished by blowing live steam into the oil.

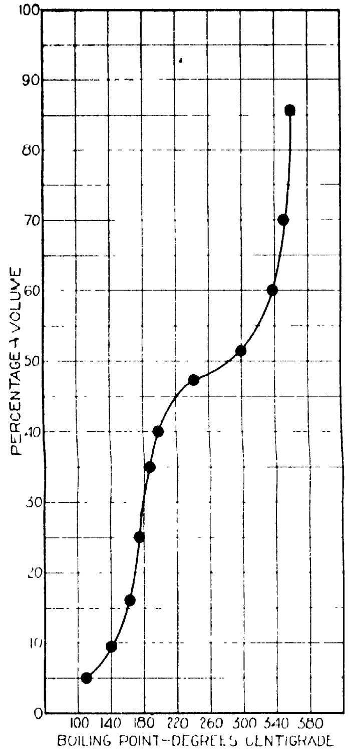

FIG. 20.—Distillation Curve of Crude Oil from Destructive Distillation of Resinous Wood.

There is another invariable law in connection with steam distillation which regulates the relative amounts of oil and water which distil at the same time. If at the time when the sum of the vapor pressures of the water and the oil reaches atmospheric pressure the partial pressure exerted by the water is twice as great as that exerted by the oil, then twice as much water as oil will distil (measuring the amounts by molecules, not by actual weight). That is, there is an invariable relation between the amounts of oil and water distilling depending only on the vapor pressures and the molecular weights of the constituents. This is the reason for the larger amounts of steam required for distilling the oils with high boiling point.

Steam distillation is convenient and is fairly efficient with low boiling oils which require only small proportions of water to make the equilibrium mixture. It is sometimes necessary in order to distil an oil from a mixture when some component of the mixture decomposes at the normal boiling point of the oil. It is very inefficient, however, for the distillation of high boiling oils, since not only must the steam furnish practically the same amount of heat required for the volatilization of the oil by straight distillation but also the heat is lost which is contained in the large quantity of steam which goes over with the oil vapors.

Another kind of steam distillation is sometimes used which may seem to be the same kind of an operation and subject to the same laws, but which works on a different principle To cut down condensation of steam in the still in which steam distillation is carried out, closed steam coils are frequently used. If these closed coils are used only enough to keep down condensation but not enough to heat the oil above its boiling point with steam, then the operation is like the steam distillation just described. If, however, the oil is heated by the closed coils to a temperature above the boiling point of water there is no liquid water in contact with the oil and *the principle of the distillation of immiscible liquids* does not hold. There is no fixed boiling temperature nor fixed proportion between water and oil in the distillate. The laws which govern here are exactly the same as those in the evaporation of water below its boiling point in a current of air. The temperature of the evaporation increases with the amount of heat furnished by the closed coils and decreases with the amount of live steam blown into the still. The proportion of oil to water in the distillate depends on the vapor pressure which in turn depends on the temperature of the oil. If the vapor pressure of the oil is say, one-fourth the total pressure in the still, then the volume of oil vapor is one-fourth and the water vapor three-fourths. By heating the oil to a higher temperature a larger ratio of oil to water can be obtained in the distillate. The efficiency of this method as determined by steam consumption is greater than that of the regular saturated steam distillation and the efficiency increases as the temperature of the distilling oil is increased.

This discussion of steam distillation has been confined to a single oil of constant boiling point, but it can now be applied to a complex mixture, such as the total oils obtained by the destructive distillation of pine wood. As in distillation without steam the lower boiling oils, or the ones with the highest vapor pressure at the temperature of the steam distillation, distil first and fractionation according to boiling points is obtained. Many people seem to have the opinion that steam distillation is a "mechanical process" and that the specific gravity of the oil is the factor which controls the fractionation, the lighter oils being carried in the current of steam more readily than the heavier oils. Since the lighter oils usually have the higher vapor pressure this opinion is perhaps excusable.

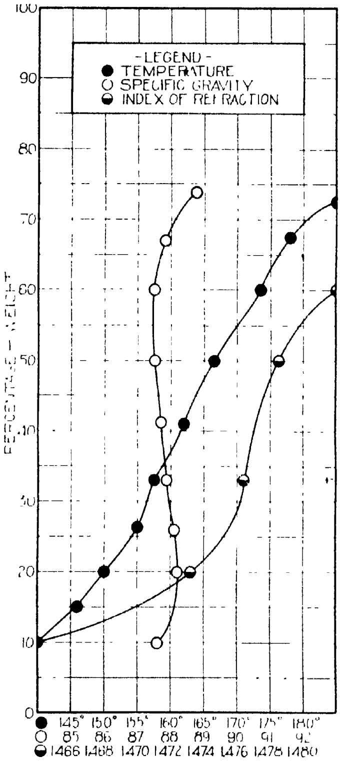

FIG. 21.—A Crude Wood Turpentine from a Destructive Distillation Process in which All the Products were Distilled and Collected Together.

On distillation of the oil whose boiling curves are shown in Figure 20 a first fraction may be obtained which has a composition indicated in Figure 21. This is a typical crude turpentine obtained from a commercial plant[1] and from it the refined wood turpentine can be obtained by a refining process consisting of chemical treatments and redistillations. Figure 21 shows that the boiling points of this crude turpentine cover a range of many degrees on both sides of turpentine (155°-180° C.), about 25 per cent boiling below 155° C. and about 30 per cent above 180° C. The specific gravity of that portion boiling between 155° to 180° C. is also very high for a pure turpentine. The fractions also were colored and had very disagreeable odors. By treating

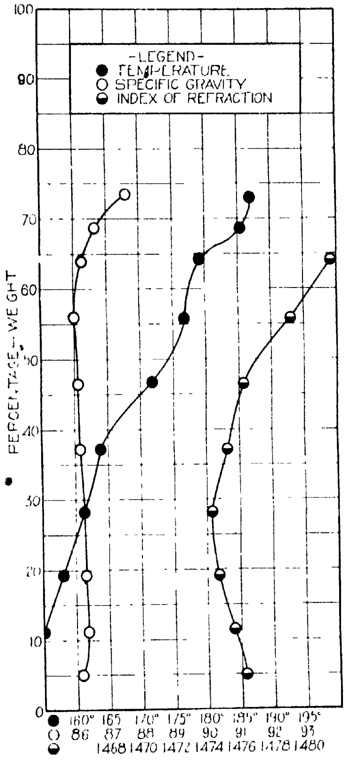

Fig 22.—The Crude Wood Turpentine of Fig. 21 after Treatment with Caustic Soda.

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[1] Forest Service Bull. 105, "Crude Turpentine No. 3," p. 40.

this crude turpentine with a solution of caustic soda the properties were changed, as shown by the distillation curves of the treated oil, Figure 22. The proportion boiling below 155° was decreased, the specific gravity of all the fractions was decreased, and the odor and color were improved. By fractional distillation of this treated crude a middle fraction of refined turpentine was obtained whose distillation curves are shown in Figure 23. This is a typical refined wood turpentine containing only a small amount of material boiling below 155° C or above 180° C. There is an odor and color in such a refined which can not be readily removed, due probably to rosin oils or oils from the de-

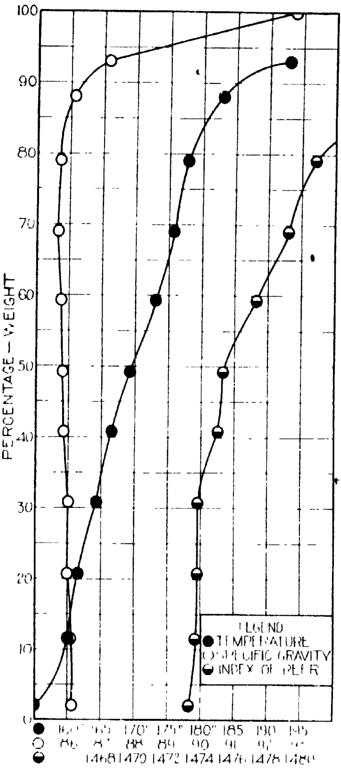

FIG. 23.—The Refined Wood Turpentine Obtained from the Treated Crude of Fig. 22 by Fractional Distillation

composition of the wood. (See composition of oils from hardwood tar insoluble in or undecomposed by caustic soda solution with boiling points between 155° and 180° C., page 74.)

In this refining process about 10 per cent of "light oils" were obtained and about 35 per cent of "heavy oils." The light oils are sometimes not separated from the turpentine, but are left in, giving a turpentine of low grade due to bad odor and low flash point. Otherwise, the "light oils" form a special product used for solvent or disinfectant purposes. The heavy oils are sometimes redistilled to give a fraction boiling between 195° C. and 240° C., called a destructive pine oil. This

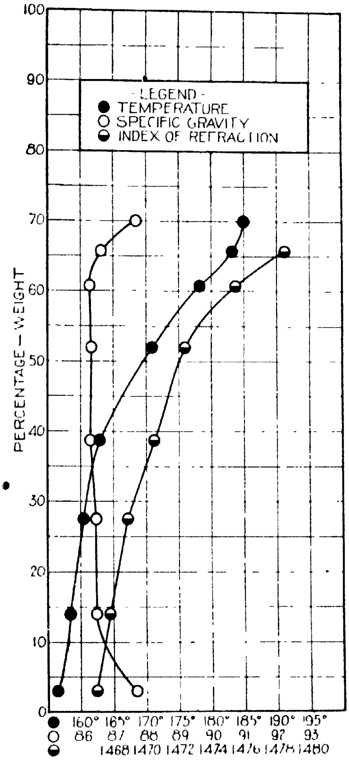

FIG. 24.—A Crude Wood Turpentine from a Destructive Distillation Process in which the Temperature was Controlled during the Distillation of the Turpentine.

heavy oil fraction may also be mixed with higher fractions distilled from the total oil to make a product called pine tar oil. Depending on the point to which the distillation of the total oil is carried, the residue left undistilled will be either a "pine tar," a soft pitch or a hard

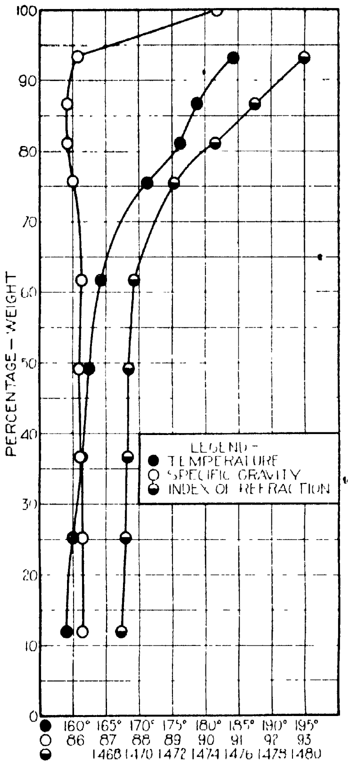

FIG. 25.—The Refined Wood Turpentine Prepared from the Crude of Fig. 24 by Treatment with Caustic Soda and Redistillation.

pitch. Often the residue left after the removal of the crude turpentine is sold as pine tar, but more oils may be removed and still have "tar" left.

There are no specifications for pine tar oil or pine tar except those of the Navy Department. These, however, are not consistent, since the pine tar oil, supposed to be distillate from pine tar, need have only 80 per cent distilling below 350° C., while the pine tar must have 87 to 90 per cent distilling below the same temperature. Klar[2] says that pine tar is commonly examined by smearing in a thin layer on a light colored wood. It should show a golden brown color, and the more rapidly it dries, the stickier it is, and the more it resists washing off with water the more valuable is the sample.

Figure 24[3] shows the distillation curves of a crude turpentine obtained by a distillation process in which some care is taken to control the temperature during the first part of the distillation and in which the crude turpentine is collected by itself instead of being mixed with the later distillates. This has much less material boiling below 155° C and the specific gravity of the fractions in the range of turpentine temperatures is lower, showing much less contamination with rosin distillation products than the turpentine produced without temperature control. This crude turpentine on treating with caustic soda solution and distilling gives a refined turpentine with distillation curves shown in Figure 25. This refined turpentine has a better odor and color than the one shown in Figure 23 and the temperature effect is also shown by the larger proportion of the pinene fraction (up to 165° C.) and the smaller proportion of the dipentene fraction (165°-180° C.) in the turpentine produced at the lower temperature (see p. 110). Although this turpentine may be of higher grade and easier to refine, yet it is usually considered that on account of the slight difference in market value the cost in increased time and increased equipment is not justified and few attempts are now made to produce such a product.

The fraction taken for chemical refining may also be taken up to a higher boiling point so as to include the pine oil, and then a refined pine oil is produced. On account of the presence of rosin oils insoluble in caustic soda with boiling points from 180° C. up, there is no sharp dividing line between the pine oil and the turpentine and the pine oil contains a considerable proportion of material not found in steam distilled pine oil. A light brown oil can be obtained, but the odor is not like that of the uncontaminated oil.

The caustic soda solution used in the chemical treatment contains various undecomposed rosin acids and also some phenols. If the pine oil fraction up to say 250° C. is given the caustic soda treatment a considerable amount of methyl ethers of phenols (see page 65) will be in the caustic soda solution. On acidifying this solution both rosin acids and phenols will be precipitated. If the pyroligneous acid is used for this acidification it is probable that a part of the dissolved tar in the acid is also precipitated, forming a mixture of rosin acids, phenols, dissolved tar and probably some neutral oil carried into solution with the alkali soluble oil or incompletely separated in the settling after the caustic soda treatment.

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[2] *Technologie der Holzverkohlung*, p. 308.

[3] Forest Service Bull. No. 105, "Turpentine No. 1," p. 34.

Pyroligneous Acid

The methyl alcohol and acetic acid occur in the pinewood pyroligneous acid in such low concentrations that it has seldom been found profitable to recover them. The proportions of acetone and methyl acetate in the crude wood alcohol are not known nor is it known whether any special difficulties in refining are encountered. The acetate prepared by the same method as hardwood acetate contains from 4 to 6 per cent more organic impurities, due apparently to certain rosin products which are volatile, soluble in water and polymerized or neutralized by lime.

Charcoal

The charcoal obtained by distillation of resinous wood has much less tendency toward spontaneous ignition than that from hardwood. Only 24 hours' cooling in closed coolers is sufficient before the final "seasoning" in the air. The reason for this is not known, but it may be due to the deposit of rosin coke in the true wood charcoal (see p. 112).

Gas

Since methyl alcohol is not one of the important products, there is no necessity for scrubbing the gas to recover it. There are probably considerable quantities of light oils in the wood gas from resinous wood, but since they are not of much value no attempt has been made to recover them.

Chapter V.

The Steam Distillation and Solvent Extraction Process.

This process has been in use for so short a time that it is not yet well standardized in details and very little literature on the subject is available. The steam distillation part of the process has, however, been studied experimentally.[1]

Steam Distillation

The theory of steam distillation of volatile oils outlined in Chapter IV applies in the removal of crude turpentine (turpentine and pine oil) from resinous wood by means of steam. There are, however, two additions that must be made to the principles previously developed to cover the effects of the presence of the wood and the rosin. The wood prevents free contact between the steam and the oils to be distilled, so that there is not a true equilibrium and the ratio of water to oil in the distillate is greater than that which would be required to distil the oil by itself. The rosin also has a similar effect, due to the fact that it lowers the vapor pressure of the oil in which it is dissolved and thus decreases the ratio of oil to water in the distillate.

Since the wood prevents free contact between the steam and the oil, the larger the pieces of wood the greater is this effect. It has been stated that the heat conductivity of wood and the penetration of wood by liquids or vapors are greatest in the direction of the grain of the wood and, therefore, the variation in size of the piece of wood to be distilled has the greatest effect in directions at right angles to the grain. Since the establishment of equilibrium between the oil and the steam is difficult on account of the protective effect of the wood, the ratio between oil and water will be varied by the speed at which the steam is blown through the wood. With a very slow current of steam almost the theoretical proportion of oil might be carried over, but with increasing speed of steam the ratio of oil to water would decrease rapidly.

It has also been shown that the steam pressure has a considerable effect on the results of steam distillation of wood, both on the total yield of oil and on the ratio between oil and water. This is not because there is any noticeable effect of steam pressure on the distillation of oil by itself but because the increased steam pressure by further penetration of steam into the wood brings better contact between oil and steam, thus increasing the total yield of oil and the oil-water ratio.

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[1] The Distillation of Resinous Wood with Saturated Steam, For. Serv. Bull. 109.

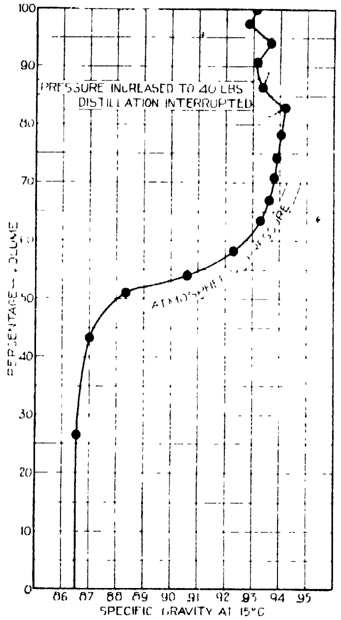

FIG. 26.—Steam Distillation of Sawdust at 0 and 40 Pounds Pressure.

Some of these effects are best brought out by Figures 26 and 27, which show the course of two experimental steam distillations under different conditions.[2] Figure 26 shows the gravity of the oil obtained during the different stages of the distillation of sawdust, at first under atmospheric pressure and later under 40 pounds steam pressure. The gravity figures are plotted against the percentages of the total oil recovered. It is seen that up to 83 per cent the distillation is much the same as if no wood or rosin were present, at least as far as the fractionation of the oil is concerned. The turpentine with gravity of 0.865 distils first, then there is a rapid rise in the gravity of the distillate until nearly pure pine oil is distilling. This indicates that the oil distilled up to this point was in contact with the steam from the start of the distillation and that the fractionation was due to the difference in boiling points between the turpentine and pine oil.

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[2] These figures are taken from For. Serv. Bull. 109, pp. 27 and 28.

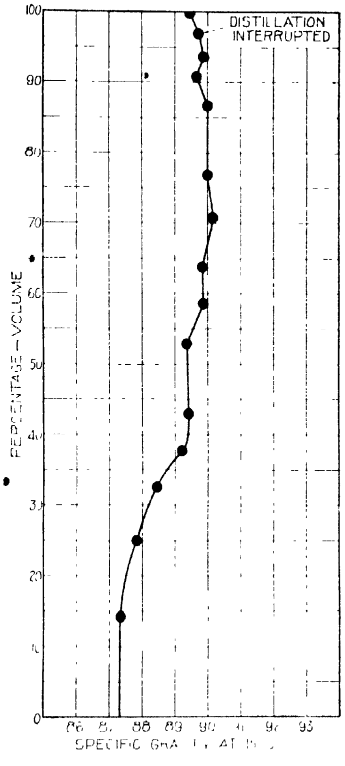

FIG. 27.—Steam Distillation of Chips 1" x 1½" x 1½" at 70 Pounds Pressure.

Beyond this point new supplies of oil were brought into contact with the steam, since the specific gravity decreases, showing that more of the low gravity turpentine is distilling which would have distilled previously if it had been in contact with the steam. These new supplies of turpentine were brought into contact with the steam first by simply stopping the distillation for a short time and second by increasing the pressure. The effect of stopping the distillation is difficult to explain, but it is to be expected that the increase in steam pressure would cause the steam to penetrate the sawdust particles to a greater distance and, therefore, come in contact with new supplies of oil.

The same effect of pressure is shown in Figure 27 which gives the gravity of the distillate during the distillation of chips 1" x ½" x ½" under 70 pounds steam pressure. In the case of the sawdust most of the oil was on or very near the surface of the fine particles and in contact with the steam from the start. With these larger chips only a small portion of the oil could be near the surface at the start and, therefore, new supplies of oil must be brought in contact with the steam from the start. This is indicated by the gravity curve which is higher than pure turpentine even at the beginning and never gets as high as pure pine oil, although there is a tendency to increase as the distillation progresses. In this case the pressure effect is caused not only by the penetration of the steam into the chips but also by the flow of the resin toward the surface of the chip, since there was some rosin collected in the bottom of the retort and the surfaces of many of the chips were covered by a thin layer of rosin. Apparently the high temperature of this distillation decreased the viscosity of the resin to the point where some flow was possible.

The general results obtained by the experimental steam distillations were:

(1) The smaller the chip the larger the yields and the higher the efficiency.[3]

(2) The higher pressures gave larger yields without lowering the efficiency.

(3) Increased speed of distillation lowered both the yield and the efficiency.

(4) Distillation at atmospheric pressure did not remove all the oil from sawdust, but 40 pounds pressure was sufficient for complete removal.

(5) Chips 1" x ¼" x ⅛" were completely distilled at 50 pounds pressure.

(6) Chips 1" x ½" x ½" were completely distilled at 70 pounds pressure.

(7) Seventy pounds steam pressure causes a slight contamination of the turpentine with low boiling oils which, however, can be readily removed by caustic soda solution.

It has been claimed that passing the steam downward through the retort was more efficient in the use of the steam and in obtaining larger yields from the wood, but this has never been investigated experimentally. It is possible that a little less steam might be used for heating the charge if passed downward since the water formed by the condensation of the steam in heating up the top of the charge to 100° C. would pass downward, give up its sensible heat to the cooler parts of the charge below, and leave the outlet in the form of a cool liquid. This would give a very slight advantage over upward distillation in which only vapor could leave the retort. It is hard to conceive, however, that any increase of yields could be obtained by this method and it is probable that the claims made for it are a reversion to the old notion of the mysterious and wonderful results from *destillatio per descensum.*

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[3] Efficiency is measured by the amount of oil brought over by a unit quantity of steam. In no case was the ratio of oil to water as high as the theoretical ratio for steam distillation under conditions of equilibrium.

This experimental work covered only the use of saturated steam and no experimental results have ever been reported on the use of superheated steam, although this has been suggested and is used commercially. So far as the removal of the oil alone is concerned it seems likely that superheated steam would have no advantage either in efficiency or total yields. The temperatures which can be used without causing contamination of the turpentine can be readily obtained by pressure steam and it is probable that some of the good effects of pressure steam, such as penetration into the chip, would not be obtained by superheated steam. Superheated steam also has a very low specific heat, so that without special means for heating the surface of the retort or preventing any radiation it would be very difficult if not impossible to blow superheated steam at say 160° C. into the bottom of a large retort and have the steam still superheated when leaving the top of the retort. In other words, the amount of available heat in superheated steam between 160° C. and say 110° C. is so small that very large quantities of steam would be required to heat the charge and distil the oil and the process would be inefficient because all the latent heat in the steam would be wasted. If the steam is heated above 160° C the charge near the steam inlet will be overheated and contamination of the turpentine will result

In steam distillation of wood previous to extraction of the rosin with volatile solvents it is more saving in steam to take out only a part of the pine oil (one-half to one-fourth) and leave the rest to be removed with the rosin by the solvent. The recovery of this residue of pine oil from the rosin requires less steam than distilling it from the wood, since, as has been stated, equilibrium conditions are not maintained when distilling from the wood and the amount of steam required is, therefore, greater than when the wood is not present. It is claimed, however, that most of the pine oil must be removed by the steam distillation or else its presence in the rosin extract will make the separation of the "nigre" incomplete.

Extraction of the Rosin

Very little is known about the fundamental principles of the rosin extraction. Gasoline is the only solvent which has been used commercially or with which experimental work has been reported, so that only this solvent will be discussed. A middle fraction of gasoline, with most of it boiling between 100° C. and 130° C., is desired, so that on one hand the losses due to the very volatile portions may be avoided and on the other hand the high boiling portions may not be present to make the solvent recovery difficult or to contaminate the pine oil which is left behind in the wood after the steam distillation.

The presence of moisture in the chips undoubtedly prevents the ready and complete solution of the rosin. When the steam distillation is finished, even when superheated steam is used, a large part of the chips are saturated with moisture and this must be removed before the extraction can be complete. This is accomplished by boiling the chips in the solvent, whereby the water is vaporized along with the solvent (principle of distillation of two immiscible liquids) and removed from the system. The commercial extraction processes obtain much lower yields than the conditions of amount of solvent and number of treatments would give if the solution of the rosin were complete in the first or even in the second or third treatment and if the extraction followed the regular counter current principle[4] after that. It must be, therefore, that many of the extraction treatments are largely useful in removing the moisture from the chip and bringing the solvent into contact with more rosin. This is a point which requires further experimental work, but such work is not promising for small scale experimentation, since it is apparently difficult to apply the results to large scale operations.

Palmer and Boehmer[5] did some small scale experimentation along the line of studying the effect of pressure on the extraction process and were able to obtain high percentage extractions, but commercial extractions are not commonly more than 75 per cent complete. It is said that a small scale extraction of the extracted chips from a commercial process with the same solvent and under the same conditions will yield very considerable additional amounts of rosin. It is difficult to suggest reasons for this incomplete extraction, unless it is the incomplete contact between chips and solvent in the large retorts used or the difficulty of removing the water from the interior of the chip, so that the solvent can come in contact with the rosin.

After the extraction is finished and the last lot of solvent is drawn off the solvent remaining on or in the chips is recovered by further steam distillation. The principles here are exactly the same as in the steam distillation for removing the crude turpentine, except that most of the rosin has been removed and the process should, therefore, be easier and more efficient. Unless the solvent contains a fraction with boiling points higher than those of crude turpentine it should be possible to remove the solvent even more completely and readily than the crude turpentine.

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[4] Discontinuous Extraction Processes, *Jour. Ind. Eng. Chem.* 9, 866 (1917).
[5] *Jour. Ind. Eng. Chem.*, Aug., 1915.

In an extraction process of this kind in which other operations besides the actual solution and washing out of rosin are carried out on the charge of wood in the same apparatus both before and after the extraction with solvent, there is a necessary relation between the time given to each of the different operations and the number of cells or extractors required.[6] This relation is expressed by the formula $n = b(2c - t) + p(2c - t - 1)$ in which

n = time required for all the operations besides the solvent action
b = time required for each boiling period
c = number of cells required
t = number of separate treatments with solvent obtained by each charge of wood.
p = time required for each pumping period

This formula applies only when the pumping of the solvent is simultaneous in all the cells. The application of this formula is shown in the following example: Suppose it is decided that an extraction process requires 6 treatments with solvent for each charge of chips, that the discharging of the extracted and steamed chips and the charging of a fresh lot will take one hour, that a turpentine distillation period of 2 hours and a solvent recovery period of 2 hours and 50 minutes will be satisfactory, and that the pumping of the solvent and the boiling periods will require 10 and 20 minutes, respectively, how many cells will be required for the process? Substituting in the equation with
$n = 60 + 120 + 170 = 350$ min.
$p = 10$ min.
$b = 20$ min.
$t = 6$
it is found that $c = 9$.

It should be noted that although *c* is an integer in this carefully selected case, a slightly longer solvent recovery period or any other change in the conditions might give a fractional value for *c*, indicating that the conditions required could not be carried out in a smoothly working process, i.e., that some part of the process would have to wait or be prolonged in order to keep in step with the rest. If, for instance, it was found that in the 9-cell process just outlined the solvent recovery was not complete in 2 hours and 50 minutes this part of the process could be lengthened only by cutting down on the time for charging, discharging, or steam distillation, by increasing the number of cells, by increasing the pumping or boiling period, or by decreasing the number of treatments. If in this case the number of cells is increased by one, the time for solvent recovery would be increased one hour with everything else the same, or if the number of treatments is decreased from 6 to 5 the time for solvent recovery can be increased by one-half hour without changing any other condition.

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[6] Hawley, Numerical Relation between Cells and Treatments in Extraction Processes, *Jour. Ind. Eng. Chem.* 12, 493 (1920).

In order to indicate in more detail the course of a complicated extraction process of this kind, Figure 28 is given which shows diagrammatically the path of the solvent and the cycle of the various operations through the extractions in the nine-cell process already outlined. The path of the solvent is indicated by arrows, the arrows pointing upward indicating the concentrated solution, leaving the system and those coming downward to a cell indicating fresh solvent coming into the system. The symbols over each cell show the operation going on in that cell as follows:

s = steaming for solvent recovery.
b = boiling.
st = steaming for crude turpentine.
d = discharging and charging.

The boiling period is 20 minutes and the pumping period is 10 minutes. For lack of space a complete cycle is not shown, but exactly one-half of a cycle is given in Figure 28 and this is enough to tell the story.

No mention has yet been made of the capacity of a battery of extractors in a system of this kind as affected by variations in the process. By studying the formula and the diagram it will be seen that the capacity of the system depends only on the size of the extractors and the time of the pumping and boiling periods. In the example given the time between two successive discharges of a cell is equal to two boiling periods plus two pumping periods and no other variable can affect this time. This is a case where increasing the number of pieces of apparatus does not affect the capacity of the system.

A similar discussion could be given on an extraction process in which, instead of pumping all the cells at one time, each cell is pumped separately, the formula could be applied and a diagram drawn, but the general principle is much the same and the details can be found in the original article on the subject.[7]

Refining

After removing the solution from the extracting system it is cooled, usually by a spray of cold water, in order to separate the "nigre" which is insoluble in the cold extract. The composition of this "nigre"

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[7] Numerical Relations, etc., *loc. cit.*

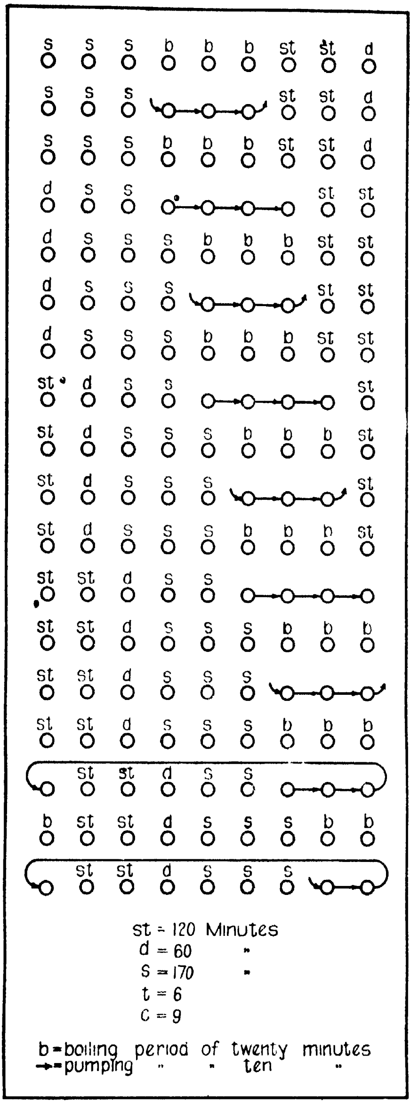

FIG. 28.—Diagram of an Extraction Process with Six Treatments in Nine Cells.

is not known and no information is available on the details of its separation. The solution now containing solvent, pine oil, and rosin is subjected to a refining process for the separation of these constituents. This consists merely of fractional distillation and is not difficult if the solvent does not contain high boiling fractions. The first part of the process is carried on more efficiently by steam in closed coils, but when the boiling point of the solution gets near that of the steam at maximum pressure live steam must be used to obtain the distillation at lower temperatures. With solvent containing no portion with boiling points above 150° C. the preparation of a pine oil (minimum boiling point 200° C.) free from solvent is easy even without column stills or redistillation, since the solvent fraction can be collected until no more solvent remains, even though some pine oil distils over. A small amount of pine oil in the solvent is no disadvantage, since it merely returns to the process and is not lost. Sometimes the solvent contains a fraction in or near the range of boiling points of pine oil, so that a complete separation can not be made. This accounts for the second grade pine oils on the market contaminated with petroleum oils.

The separation between the pine oil and the rosin is also simple, since it is a separation of a volatile from a non-volatile material. Here is a good example of an operation in which steam distillation or some similar method of lowering the boiling point is a necessity. The normal boiling points of the oil are as high as the decomposition temperature of the rosin and at the end of the operation, when there is only a little high boiling oil present in a large amount of rosin, the boiling points are very much higher than the normal. Under these conditions steam distillation is required even though large amounts of steam are necessary to bring over the last traces of oil. During the steam distillation the closed coils are used not only to increase the efficiency (see p. 115) but also to keep the rosin sufficiently liquid so that it will not foam and can be drawn off readily at the end of the operation.

The crude turpentine obtained by the steam distillation of the chips requires only fractional distillation for its refining unless there has been a little contamination due to high temperatures, in which case a treatment with a small amount of caustic soda solution before distillation is all that is required in the way of chemical treatment. The highest boiling turpentine constituents, dipentene and cineol, boil at 176° C. and the lowest boiling pine oil constituent, fenchyl alcohol, boils at 202° C., so that there should be no great difficulty in separating them. By steam distillation in a simple still without a column it is not possible to make a complete separation and, therefore, redistillation of one fraction from the first distillation is necessary.

One of the difficulties with this extraction process using a petroleum oil solvent has always been the loss of solvent. The pumping and boiling of the large quantities of hot volatile solvent required by this process has led to losses which in some cases were large enough to make one of the major expenses of the process. Either too high or too low boiling fractions in the solvent will increase the loss, the first on account of high volatility and difficulty in complete condensation, the second on account of difficulty in removing from the extracted chips by the steam distillation. It has been a common opinion that most of the solvent loss consisted of oil remaining on the chips, but as has been shown there should not be so much difficulty in removing a solvent of boiling points below 150 from the chips as there is in distilling the turpentine fraction, and this is accomplished practically completely. In fact, there is only one place in the present process where loss is unavoidable aside from the small losses always occurring from leaks and incomplete condensation. This is at the time when the solvent is first brought in contact with a fresh charge of wood.

The spaces between the chips and above and below the charge are filled with air and the air is forced out as the solvent comes in. This air will be nearly saturated with solvent at the temperature at which it escapes. If the air escapes at the temperature of the incoming hot solvent the loss will be considerable, but if the air is passed through a condenser the loss from this source should not be great. Usually after the first boiling with solvent the extractor is filled with vapor above the solvent and pumping solvent from one extractor to another is accomplished without the escape of air saturated with solvent. It is believed, therefore, that the loss of solvent does not occur in only one or two of the operations but that it is made up of the very numerous small lossses incident to the handling of such large volumes of hot volatile material.

Combination of Extraction Process and Pulping Process

It has been so often suggested that the chips from an extraction process should be used for making paper pulp, that this subject will be discussed briefly. This combination of two processes using the same raw material seems ideal and it is believed to be merely a matter of custom and prejudice which has prevented its accomplishment. The men in charge of the extraction plants have been accustomed to preparing their wood for the process by a method which is comparatively simple, "hogging" and "shredding," and which gives a chip apparently suitable for the distillation and extraction operations. These chips are, however, so irregular in shape and size that no pulp mill operator would consider using them even if they could be obtained without expense. The pulp mill operator is accustomed to a carefully prepared chip which is fairly even in size, especially in the important dimension, its length with the grain. There is no other important point which stands in the way of this combination of processes. Longleaf pine stumpwood is a suitable raw material for making pulp by the sulphate process and no necessary operation of the extraction process need injure its quality for this purpose. The frequently charred outside portions of the stumpwood might be expected to injure the quality of the wood made from it, but it is surprising how much of this charred wood is lost in the chipping and extraction processes and how little the remaining portion affects the quality of the paper. If necessary also the charred wood can be largely separated before chipping. Some of the wood from commercial extraction plants which has been examined by pulp men has been condemned, and properly so, on account of discoloration or even incipient charring by the superheated steam used in the solvent recovery operation. It has been shown that the use of superheated steam at this stage of the process is not necessary and that as good or better results could be obtained by saturated steam at temperatures low enough to avoid any effect on the wood fiber. Even admitting that all the solvent can not be removed by saturated steam, the remainder could readily be recovered during the cooking process in the manufacture of the pulp.

If these points are allowed the only concession that the extraction process must make is in the size and shape of chip. No experimental work has been reported on the effect of length of grain of chip on the recoveries of rosin by extraction, but there is no doubt that pulp chips ⅝″ in length would be entirely satisfactory for the steam distillation process. It has been stated that any process requiring penetration of a chip by vapor or liquid is affected more by the size of the chip with the grain than in any other direction. Many of the ordinary extraction chips prepared by hogging and shredding, although they look smaller than chips prepared on a pulp chipper, are longer with the grain than the pulp chips. These chips are probably not so good for extraction as pulp chips would be and it is likely that evenly chipped wood ⅝″ with the grain would be as good as the average chips prepared for extraction so far as the size is concerned. It is also probable that the pulp chips would be even better than the extraction chips from the standpoint of circulation of the solvent. The tendency for the extraction chips to pack together and prevent free circulation of the solvent is due to the irregular shapes and uneven sizes and this would be largely avoided with the regular pulp chips.

These points indicate that with very little concession on either side a combination process could be arranged so that one part could obtain a valuable raw material from what the other part would otherwise use only as fuel.